

N. F. VOZNAYA

# Chemistry of Water & Microbiology

Mir Publishers Moscow

## **Chemistry of Water and Microbiology**

**N. Voznaya**

This is the second printing of this book. Compared with the first one, which appeared in 1967, the new book has been significantly revised and enlarged. The changes mainly concern the theory of the microbiology in particular.

The structure of the book is as follows: the first chapters deal with the theory of solutions, kinetics of chemical reactions, oxidation-reduction processes, colloid solutions and their properties.

Next, the book discusses the physical and chemical properties of natural waters and effluents, and the latest advances in methods of their purification and decontamination. Special emphasis is laid on the role of microorganisms in these processes.

The book is intended for high school students, majoring in water-supply and sewage engineering.



Н. Ф. ВОЗНАЯ

# **ХИМИЯ ВОДЫ И МИКРОБИОЛОГИЯ**

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# Chemistry of Water & Microbiology

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by Alexander Rosinkin

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# PREFACE

This book deals with the theory and practice of the treatment of natural waters and sewage. The problems discussed will help experts in the field of water-supply and sanitation to predict new trends of the processes involved, to assess their efficiency, and to choose the most suitable method.

The objects of this course are as follows:

(a) acquainting students with modern concepts of the physico-chemical processes occurring between various substances contained in natural waters and sewage;

(b) acquaintance with the principles of analysis of natural waters and sewage and with the utilization of the results obtained to assess the quality of water, to choose the right method of purification, and to predict the effect of water on building materials and structures;

(c) acquaintance with modern methods of treatment of natural waters and sewage and their disinfection;

(d) providing generalized concepts of bacteriological and biological analyses of waters and biological methods of the treatment of sewage.

This is the second edition of the book. It has been revised and enlarged significantly. The section "Microbiology" has in particular been enlarged.

The author takes this opportunity to express her gratitude to T. L. Simakova, Doctor of Biology, for her valuable assistance in the section "Microbiology", and also to Candidates of Science, L. B. Dolivo-Dobrovolsky, M. F. Rodicheva, and I. N. Churbanova for reading the manuscript and giving some useful advice.

*Nadezhda F. Voznaya*



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# CONVERSION OF SOME UNITS USED IN THIS BOOK

Definition	Units	SI units	Conversion factor
<i>CGS System</i>			
Mass	g	kg	$10^{-3}$
Length	cm	m	$10^{-2}$
Force	dyne	n	$10^{-5}$
Surface tension	dyne/cm erg/sq. cm	N/m J/sq. m	$10^{-3}$ $10^{-2}$
Viscosity	centipoise	$N \times \text{sec} \times m^{-2}$	$10^{-3}$
<i>Arbitrary Units</i>			
Dipole moment	$10^{-18}$ el. st. units $\times$ cm	$m \times \text{sec} \times A$	$0.333 \times 10^{-29}$
Osmotic pressure	atm	N/sq. m	$1.0133 \times 10^5$
Pressure	mm Hg atm	N/sq. m N/sq. m	$1.333 \times 10^2$ $1.0133 \times 10^5$
Specific conductance	$\text{Ohm}^{-1} \times \text{cm}^{-1}$	$\text{Ohm}^{-1} \times m^{-1}$	$10^2$
Heat	calorie	J	4.187
Heat capacity	$\text{cal} \times \text{mole}^{-1} \times \text{deg}^{-1}$	$J \times \text{kmole}^{-1} \times \text{deg}^{-1}$	$4.187 \times 10^3$
Thermal conduction	$\text{cal/cm} \times \text{sec} \times \text{deg}$	$J \times m \times \text{sec}^{-1} \times \text{deg}^{-1}$	$4.187 \times 10^2$
Radius	Å	m	$10^{-10}$
Entropy	$\text{cal} \times \text{deg}^{-1} \times \text{mole}^{-1}$	$J \times \text{deg}^{-1} \times \text{kmole}^{-1}$	$4.187 \times 10^3$
Enthalpy	kcal $\times$ mole $^{-1}$	J $\times$ kmole $^{-1}$	$4.187 \times 10^6$
Work performed by a system	l-atm $\times$ mole $^{-1}$ kcal $\times$ mole $^{-1}$	J $\times$ kmole $^{-1}$ J $\times$ mole $^{-1}$	$1.0133 \times 10^6$ $4.187 \times 10^6$
Gibbs free energy	kcal $\times$ mole $^{-1}$	J $\times$ kmole $^{-1}$	$4.187 \times 10^6$
Volume	l	cu. m	$10^{-3}$
Molality, molal concentration	$\text{mole} \times g^{-1} \times 10^{-3}$	$\text{kmole} \times \text{kg}^{-1} \times 10^{-3}$	1.0

## Important Physical Constants

Universal gas constant,  $R = 8.315 \times 10^3$  J/kmole  $\times$  deg  
 Boltzmann constant  $K = 1.38 \times 10^{-23}$  J/deg  
 Avogadro number,  $N_A = 6.024 \times 10^{26}$  kmole $^{-1}$   
 Faraday number,  $F = 9.65 \times 10^7$  C/kg-equiv

# INTRODUCTION

The reserves of water on the Earth are immense, but this is mostly salt water which is unfit for drinking or irrigation purposes. The amount of fresh water is huge as well but its distribution over the globe is uneven. There are zones where the yearly precipitation exceeds the amount of water evaporated from the surface of the Earth, and conversely, areas are known where the amount of moisture evaporated is greater than the yearly precipitation.

The water demand for drinking and other domestic needs in a modern town varies from 100 to 500 litres a day per capita. But water is also consumed in industry and agriculture (irrigation, cattle breeding), and if the total water demand is thus considered, it increases 10-12 times per capita.

As man uses water, he pollutes it inevitably, and when the water is returned to the open bodies it contaminates natural water.

Water supply and sewage treatment were in a deplorable state in pre-revolutionary Russia. And it was only after the Great October Socialist Revolution that municipal and industrial water-supply systems were launched on a wide scale. Special reagents have been devised to treat water and researchers are now looking for methods by which water could be treated without any reagents (by ultrasound coagulation, magnetic treatment, electric discharge, electrophoresis, etc.).

The quality of water is now the concern of experts in all countries of the world. The decision of WHO's 29th session (May 1976) emphasizes that water delivered to the consumer should meet the high requirements of modern hygiene and should at least be free from pathogenic organisms and toxic substances.

The quality of water depends on the location of the source and the state of environmental protection in a given area.

The official movement of the environmental protection in the USSR was started in 1924 when the National Society of Protection of Nature was founded. The movement later spread from the Russian Federation to all the Republics united in the USSR. This spread was favoured by the incessant concern of the Soviet Government and the Communist Party.

All possible measures are being taken in the USSR to preclude the ingress of toxic substances into water bodies. But Thor Heyerdahl justly notes that there are no 'national waters' in the ocean, they are constantly moving, and while nations can divide the bottom of the ocean, they can never divide waters running above it. Sea currents do not mind political or national frontiers. Water constantly moves in the world ocean to transport poisons from one region of the globe to another. For example, DDT was used in the fields of East Africa but in a few months it was revealed in the water of the Bay of Bengali, i.e. at a distance of 6,000 km. Hence the pollution control should be the object of great and incessant concern of all nations.

All effluents should be treated thoroughly before disposal. It is expedient that they should be reused as much as possible for all purposes where water of lower quality can be used. Even purified effluents can pollute water and they should be discarded only on the condition that no other reasonable use of them seems to be feasible.

Special attention should be paid to the search for methods of treating industrial effluents with raw and waste materials used in a particular industry.

All processes involved in the treatment of water and effluents are connected with physico-chemical and micro-biological conversions, and water-supply and sewage engineers must study and use them rationally to control water pollution.

## CHAPTER ONE

# WATER AND AQUEOUS SOLUTIONS

---

### 1.1. Water

**The Internal Structure of The Water Molecule.** The water molecule consists of hydrogen and oxygen. According to modern concepts of the atomic structure, the electron clouds in water molecules form an irregular tetrahedron. The oxygen atom assumes the central position and the two hydrogens are in the opposite angles of one of the cube faces. The hydrogens are arranged at an angle of  $104^{\circ}31'$ . Two of the eight electrons of the oxygen atom are found around the nucleus, two are bound with the hydrogen atoms, and two unshared pairs of electrons form branches arranged in the opposite direction with respect to the electron clouds of the hydrogens (Fig. 1.1). These cloud branches are the regions of concentration of negative charges and account for the hydrogen bonding between water molecules and other substances. The water molecule can also be described in terms of groups of electron orbitals (Fig. 1.2).

The electronic configuration of the second layer of the free oxygen atom is as follows:  $2s^2$ ,  $2p_z^2$ ,  $2p_y'$ ,  $2p_x'$ ; the charge density of the  $2s^2$  electron pair is distributed in the sphere to the side of the inner electron shell, while the density of the charge of  $2p_z^2$ ,  $2p_y$ ,  $2p_x$  electrons is distributed symmetrically about the mutually perpendicular axes  $x$ ,  $y$ , and  $z$ . As the two hydrogens become bonded by  $2p_y$ - and  $2p_x$ -orbitals, the  $90^{\circ}$  angle increases due to electrostatic repulsion, this disturbance increasing hybridization. The valency angle, corresponding to the minimum potential energy of the molecule, and passing through the maximum electron density, increases with the participation of  $s$ -electrons in the valency state. The hybridization of  $p$ - and  $s$ -states stimulates redistribution of the charge on two unshared electron pairs of the oxygen atom to favour unsymmetrical removal of the charge from the oxygen nucleus in the direction away from the protons.

As the charge is distributed, a significant dipole moment (1.84 debye) arises in the molecule. This important parameter, and also the angle and the length of the bond are shown in Fig. 1.3.

If water molecules had no negatively charged branches of the electron cloud and the dipole moments, they could not interact between one another.

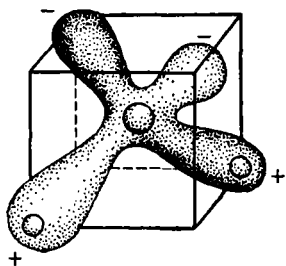


Fig. 1.1. The electron cloud of the water molecule

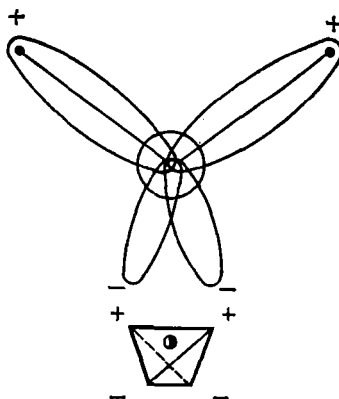


Fig. 1.2. The electron orbitals of the water molecule

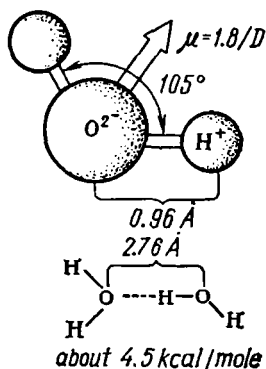


Fig. 1.3. The structure of the water molecule and the hydrogen bond

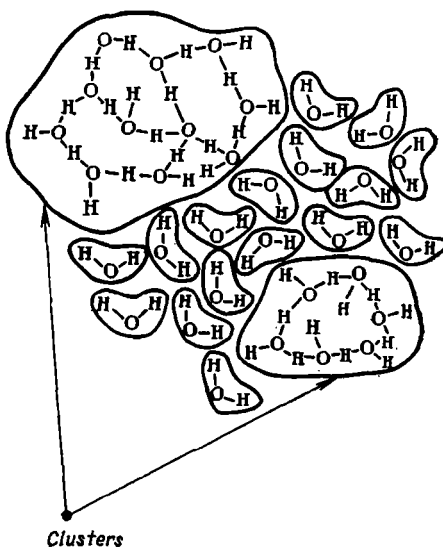


Fig. 1.4. The structure of liquid water in Frank-Wen flickering clusters

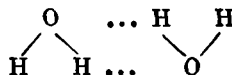
**The Structure of Liquid Water.** Various models have been proposed to explain the abnormal properties of water in the liquid state. Most of these show liquid water as a crystalline substance (liquid crystals). The ordered (crystalline) arrangement of particles in liquid water has been proved experimentally. As ice melts, its lattice is partly disrupted and the voids and the open structure of ice are filled with the liberated water molecules. The density of

liquid water thus increases. It has been found that the amount of unbound molecules that fill the voids in the liquid water at 0°C is about 16 per cent of the total number of molecules.

Of special interest is the model which shows the structure of liquid water as flickering clusters\* (Fig. 1.4), consisting of molecules interconnected by the hydrogen bonding and floating in more or less "free" water. Clusters are always present in fluid liquids, where they incessantly form and break up in accordance with the random thermal changes in the microparticles of the liquid. Frank and Wen have determined the half-life period of clusters, at  $10^{-10}$ - $10^{-11}$  second, which corresponds to the time of relaxation processes in water. This time is 100-1000 times greater than the period of molecular oscillations.

The classical theory of the structure of water by Bernal and Fowler claims that its maximum density is found at 4°C because at this temperature most molecules are bound in a quartz-like structure, while at other temperatures they have a tridymite-like crystalline structure producing a lower density.

Water molecules are characterized by *hydrogen bonding*. This is explained by the property of the hydrogen atom of interacting with a strongly electronegative element, for example, with the oxygen of another water molecule. As the hydrogen atom donates its only electron for a covalent bond with oxygen, it turns into a very small nucleus, almost devoid of the electron shell. For this reason it is not repelled by the electron shell of the oxygen of another water molecule, but on the contrary, is attracted to it and can interact with it. The greatest stability is found in twin molecules ( $H_2O$ )<sub>2</sub> formed with two hydrogen bonds:



(the dots indicate the hydrogen bond).

It should be noted that according to the existing concept of the hydrogen bond, it cannot be regarded as purely electrostatic.

According to the molecular orbital method, the hydrogen bond is formed by the dispersion forces, covalent bonding, and electrostatic interaction.

**The Isotopic Composition of Water.** Water is the product of the combination of two chemical elements, viz., hydrogen and oxygen. Both have isotopes.

Three isotopes are known for hydrogen: protium  $^1H$ , having the mass of 1.007822 carbon units; deuterium  $^2H(D)$ , 2.0141; and tritium  $^3H(T)$ , 3.017001. The last is formed during nuclear decay.

---

\* Supramolecular complexes consisting of many molecules are called clusters.

The content of D in the natural mixture of hydrogen isotopes is 0.014-0.015 per cent.

Three isotopes are known for oxygen as well. Their mass numbers are 16, 17, and 18. Their proportions in the natural mixture of the isotopes are 2670:1:5.

Natural water is a mixture of molecules having the following formulas:  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $\text{HD}^{16}\text{O}$ ,  $\text{HD}^{17}\text{O}$ ,  $\text{HD}^{18}\text{O}$ ,  $\text{D}_2^{16}\text{O}$ ,  $\text{D}_2^{17}\text{O}$  and  $\text{D}_2^{18}\text{O}$ .

Water with the chemical formula  $\text{D}_2^{16}\text{O}$ ,  $\text{D}_2^{17}\text{O}$  and  $\text{D}_2^{18}\text{O}$  is known as heavy water, while water containing tritium is called super-heavy water,  $\text{T}_2\text{O}$ .

Heavy water is obtained by the prolonged electrolysis of natural water. It is more difficult to electrolyze than ordinary water and therefore concentrates in the cell because the deuterium ion loses its charge much slower than the protium ion.

The properties of heavy water are markedly different from those of common water. It freezes at  $3.8^\circ\text{C}$ , boils at  $101.4^\circ\text{C}$ , its density at  $20^\circ\text{C}$  is  $1.1059\text{ g/cc}$ . Its maximum density is at  $+11^\circ\text{C}$ . Salts are less soluble in heavy water. It produces an inhibiting action on vital processes in plants and animals. It is used as a moderator in nuclear fission processes.

Super-heavy water  $\text{T}_2\text{O}$  has the following (approximate) constants: m.p.,  $+9^\circ\text{C}$ ; b.p.,  $104^\circ\text{C}$ ; density,  $1.33\text{ g/cc}$ .

Hence water is a mixture of nine different molecules. Therefore none of the properties of water, especially its density, are constant, but instead depend on the proportion of each component in the mixture. For example, compare the densities of water obtained from various sources:

	(at $4^\circ\text{C}$ )
Snow water	0.9999977
Rain water	0.9999990
River water	1.0
Ocean water	1.0000015
Water of a living body	1.0000012
Water of plants	1.0000017
Water of crystallization in minerals	1.0000024

Although the difference in the densities of pure water of various origins is comparatively small, it can be reliably measured on instruments.

**The Physical Properties of Water.** Pure water is a colourless (in thin layers) or bluish-green (in thick layers) clear liquid having neither odour nor taste.

*The mass of 1 ml of purified river water is assumed to be the unit of mass and is known as a gram.*

Some physico-chemical properties of water are given below:

Electrical conductivity at $18^\circ\text{C}$	$4.3 \times 10^{-8}\text{ ohm}^{-1} \times \text{cm}^{-1}$
Freezing point at 760 mm Hg	$0.00^\circ\text{C}$

Boiling point	100.00°C
Dielectric constant:	
at 0°C	88.3
at 18°C	81.0
Thermal conductivity*	$0.00143 \text{ cal} \times \text{cm}^{-1} \times \text{sec}^{-1} \times \text{deg}^{-1}$

The thermal conductivity of water is insignificant compared with that of other substances. For example, the thermal conductivity of cork is  $0.1 \text{ cal} \times \text{cm}^{-1} \times \text{sec}^{-1} \times \text{deg}^{-1}$ , of asbestos 0.3-0.6, of concrete 2-3, of wood 0.3-1.0, of brick 1.5-2.0 and of ice  $5.5 \text{ cal} \times \text{cm}^{-1} \times \text{sec}^{-1} \times \text{deg}^{-1}$ .

The low thermal conductivity and high heat capacity of water account for its wide use as a heat carrier. Because of the high heat capacity water cools slowly in winter and slowly warms up in summer, to serve as a natural temperature regulator for the globe.

Pure water is also characterized by some other properties which differ greatly from those of other substances in nature. These special properties are known as the *abnormalities* of water. They are as follows.

1. As water is heated from 0 to 4°C its volume does not increase but, on the contrary, contracts, and water thus attains its maximum density not at its freezing point (0°C) but at 4°C (more accurately, 3.98°C).

2. As water is frozen it expands instead of being contracted, as with all other substances, and its density decreases.

3. The freezing point of water decreases with increasing pressure (instead of increasing, as one might expect).

4. The specific heat of water is extraordinarily high compared with that of other substances.

5. Due to the high dielectric constant, water is a better solvent and dissociating agent than other liquids.

6. Water is characterized by the highest surface tension\*\* of all liquids, viz.,  $75 \text{ erg} \times \text{cm}^{-2}$  (that of glycerol is  $65 \text{ erg} \times \text{cm}^{-2}$ , of ammonia 42, and of all others below  $30 \text{ erg} \times \text{cm}^{-2}$ ). The only exception is mercury:  $436 \text{ erg} \times \text{cm}^{-2}$ .

Surface tension and density are decisive for the height to which a liquid can rise in a capillary system as it filters through a porous obstacle.

All the abnormalities are explained by the specific structure of the water molecule and its ability to form molecular aggregations, or associates  $(\text{H}_2\text{O})_n$ .

---

\* Thermal conductivity is determined by the coefficient of thermal conductivity, i.e. the amount of heat in calories which passes in a second through a square centimetre of a 1 cm thick plate when the temperature difference is 1°C.

\*\* Surface tension is the value characterizing the state of the surface of a liquid, equal numerically to the work done to form a unit surface; measured in  $\text{erg} \times \text{cm}^{-2}$ .

For example, the high heat capacity of water can be explained by the decomposition of the associated molecules on heating. Since this process is associated with the consumption of energy, the heat is spent not only in raising the temperature of the water but also to destroy the molecular associates.

**The Chemical Properties of Water.** Water is a highly reactive substance. It reacts with oxides of metals and of nonmetals to form basic and acid hydrates. Water has amphoteric properties. With alkalis, it acts like an acid and with acids behaves like a base. Active metals react with water to liberate hydrogen. For example, potassium and sodium decompose water without heating, magnesium with heating, and iron with strong heating. The water molecule has negatively charged branches of the electron cloud and it can therefore be a ligand in coordination compounds (with the formation of donor-acceptor bonds)  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ .

Water reacts with some salts to cause exchange decomposition (hydrolysis).

---

## 1.2. The Theory of Solutions

A knowledge of the theory of solutions is necessary for the successful purification of natural waters and effluents. The discussion in this section will help one to understand the essential processes occurring between various substances in water, to determine the behaviour of water pollutants in specific conditions, and give a correct assessment of the quality of water from various sources, so that the most rational and efficient methods of treatment can be selected.

**Disperse Systems.** If a substance is distributed as the minutest particles in any other substance, the system is called *dispersed*. Depending on the state of aggregation of the dispersed substance and the medium in which it is distributed, nine types of disperse systems can be distinguished (Table 1.1).

The properties of disperse systems, their stability in the first instance, depend on the size of the distributed particles. The particles in coarse systems are very large (over  $1 \times 10^{-4}$  mm) compared with the size of a molecule. Such systems are unstable: the dispersed substance quickly settles or floats to the surface. These are *suspensions*. Depending on the state of aggregation of the dispersed substance, disperse systems can be classified as *true suspensions* and *emulsions*.

Suspensions are formed by dispersing solid particles through a liquid medium, while emulsions consist of two (or more) liquids which do not normally dissolve each other and which separate on standing.

Table 1.1

## Disperse Systems

Dispersed matter	Dispersion medium	Symbol	Examples
Gas	Gas	$g+g$	Mixture of gases
Liquid	Gas	$l+g$	Fog
Solid	Gas	$s+g$	Smoke
Gas	Liquid	$g+l$	Oxygen in water
Liquid	Liquid	$l+l$	Alcohol in water
Solid	Liquid	$s+l$	Salt in water
Gas	Solid	$g+s$	Hydrogen solution in palladium
Liquid	Solid	$l+s$	Pearl (droplets of water dispersed in calcium carbonate)
Solid	Solid	$s+s$	Solid solutions (alloy of gold and silver in the solid state)

If the particles of solid matter are reduced to the size of a molecule ( $1 \times 10^{-6}$  mm), the highly disperse system becomes very stable and does not separate even after indefinite standing. Such disperse systems are known as *molecular* or *true solutions*, or simply *solutions*\*.

Colloid systems are intermediate between suspensions and molecular solutions (particle size from  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  mm). Colloid systems are quite stable provided the conditions remain invariable.

Hence any solution consists of a solute and a solvent. It is often difficult to distinguish between them and to decide which is the solvent and which the solute. By convention, the substance which is present in excess is called the 'solvent'. For example, in a 10 per cent alcohol solution alcohol is the solute and water is the solvent. A 96 per cent alcohol solution contains water as the solute while alcohol is the solvent.

Molecular solutions are intermediate between chemical compounds and mechanical mixtures. The uniformity of solutions and the variation of the heat effect of dissolution bring them into the class of chemical compounds, while the variation of concentration of a solute within a wide range gives grounds to describe them as mechanical mixtures.

\* A solution is an energetically stable homogeneous (single-phase) condensed system of continuous variable composition formed by several components which are uniformly distributed throughout one another and are in a state of dynamic interaction.

The general regularities which could define the quantitative aspect of solubility have not been established. The only thing that can guide us is the empirically derived rule: like dissolve in like. In terms of modern concepts of molecular structure, this rule can be interpreted thus: if the molecules of the solvent are polar, they will readily dissolve polar and ionic molecules and will with difficulty dissolve substances with nonpolar molecules and vice versa.

**Solubility of Gases in Liquids.** The solubility (absorption) of gases in liquids is variable. For example, in normal conditions, one volume of water can dissolve 0.02 volume of hydrogen, 400 volumes of HCl and 700 volumes of  $\text{NH}_3$ .

Most gases dissolve in less polar solvents better than in water.

The solubility of gases increases with decreasing temperature and decreases with increasing temperature. Therefore, as a liquid is boiled, virtually all dissolved gases are removed from it.

The solubility of gases in liquids obeys the Henry-Dalton law: *at constant temperature the solubility of each component of a gas mixture in a given liquid is directly proportional to its partial pressure\* over the liquid and does not depend on the total pressure of the gas mixture or the content of other components* (i.e. each gas is dissolved as if it were alone in a given volume). For example, water, on contact with air, dissolves the same volume of oxygen that it would dissolve on contact with pure oxygen at a pressure of 0.2 atm (partial pressure of oxygen in air).

The solubility of gases varies strongly with pressure. By solubility of a gas we mean here the mass of a gas which saturates a given volume of a liquid at a given pressure of the gas over the solution.

An example that well illustrates the Henry-Dalton law is carbonated water, which is a saturated solution of carbon dioxide in water, prepared at a pressure of several atmospheres. As it then comes in contact with air, in which the partial pressure of  $\text{CO}_2$  is only 0.2 mm Hg, the dissolved carbon dioxide is liberated in the form of gas bubbles. The mathematical expression of the Henry-Dalton law is

$$g = kp$$

where  $g$  is the weight of gas dissolved per unit volume in mg/litre,  $k$  is the Ostwald solubility coefficient (constant value), and  $p$  is the partial pressure of the gas over the solution in mm Hg.

The universally used solubility coefficient is the Bunsen absorption coefficient  $\alpha$ . The Bunsen coefficient for the solubility of gas in liquid at a given temperature is equal to the volume of the gas measured at  $0^\circ\text{C}$  and at a pressure of 1 atm.

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\* Partial pressure is the contribution of each constituent in a gas mixture to the total pressure.

The solubility coefficients  $k$  and  $\alpha$  depend on the nature of the solute gas and solvent, and special coefficients are therefore used for each gas and solvent (see Table 1.2).

Table 1.2  
Solubility of Oxygen in Water at 25°C

Pressure, $p$ , mm Hg	Solubility, $g$ , mg/l	$\frac{g}{p} = k$	Solubility coefficient $\alpha$ , mg/ml
175	9.5	0.0543	0.0065
202	10.7	0.0530	0.0075
300	16.0	0.0533	0.0112
414	22.0	0.0531	0.0154
610	32.5	0.0533	0.0227
760	40.8	0.0537	0.0283

The quantitative dependence between the solubility of gas and temperature is expressed by the Clapeyron-Clausius equation

$$\ln \frac{N_2}{N_1} = -\frac{\lambda}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where  $N_2$  and  $N_1$  are solubilities of gases at temperatures  $T_2$  and  $T_1$ ;  $\lambda$  is the molar heat of dissolution;  $T_2$  and  $T_1$  are temperatures in K; and  $R$  is the universal gas constant.

The presence of salts in water decreases the solubility of gases in it. This dependence was established experimentally by the Russian physiologist I. M. Sechenov

$$\log \frac{N_0}{N} = KC$$

where  $N_0$  and  $N$  are the solubility of gases in pure water and a salt solution with concentrations  $C$  mole/litre respectively, and  $K$  is the Sechenov constant (for its value for various gases see the Appendix).

**Mutual Solubility of Liquids.** The mutual solubility of a liquid varies over a wide range. For example, alcohol and water are miscible in any proportion, while water is practically immiscible with benzene. In most cases we deal with partial mutual solubility, as in the case with the system water—ether.

The mutual solubility of liquids changes with heating, but in some cases it increases and in others decreases.

The main regularities of the mutual solubility of liquids were established by V. F. Alexeyev in 1876. From his vast experimental data he established that a two-layer system is formed by mixing two liquids having limited solubility, while the composition of each layer in the system at equilibrium *remains invariable at con-*

*stant temperature.* As the ambient conditions change, the composition of the layer changes as well. An increase in temperature often increases the mutual solubility of liquids. The temperature above which liquids become completely miscible with each other in any proportion is called the *upper critical solution temperature* or the *upper consolute temperature*. The system aniline—water is a good example (Fig. 1.5). The graph shows the dependence of the composition of equilibrium layers of liquids with partial solubility on temperature. The curve *ABC* is known as the *separation curve*. It separates the homogeneous and heterogeneous parts of the system. Any point in the region bounded by the curve and the axis of the abscissas (shaded part) corresponds to the two-layer system. The region beyond the curve corresponds to the one-layer system.

Points *A'-A''* on the curve represent the composition of equilibrium layers at a given temperature. The straight lines connecting the points of the conjugate (equilibrium) layers (*A'* and *A''*) are called *tie lines* or *conodes*.

Alexeyev derived a rectilinear diameter rule according to which *the mean arithmetic of the composition of the equilibrium liquid phases is a linear function of temperature, and the point of intersection of this line with the equilibrium curve corresponds to the critical temperature of the solution.* All points on the straight line *BD* (Fig. 1.5) are located in the middle of the points corresponding to the composition of equilibrated liquid layers. For example, the abscissa of point *A<sub>0</sub>* is equal to the half-sum of the abscissas of points *A'* and *A''*.

The mutual solubility of liquids in some systems increases with decreasing temperature and the liquids can dissolve completely in one another. The temperature below which the components in any proportion become miscible is known as the *lower critical temperature of the solution*.

There are systems with upper and lower consolute temperatures, for example the system water—nicotine. This system is shown graphically in Fig. 1.6.

The mutual solubility of liquids at constant temperature depends on the presence of impurities. For example, if potassium chloride is added to a homogeneous liquid system phenol—water (at 339°C) the system will separate into layers. This is explained by the fact that *KCl* is soluble only in water and it therefore quickly displaces phenol from the aqueous layer and its solubility in water decreases. But this system can be returned to the homogeneous state by raising the temperature. The critical temperature of the system phenol—water increases 30° at the concentration of *KCl* of 3 per cent. A homogeneous system ethyl alcohol—water likewise separates into layers on the addition of potassium carbonate. The upper layer will be, almost completely, ethyl alcohol, while the lower layer will consist of an aqueous solution of *K<sub>2</sub>CO<sub>3</sub>*.

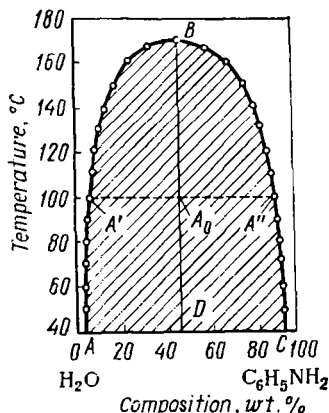


Fig. 1.5. Mutual solubility of water and aniline (V. F. Alexeyev)

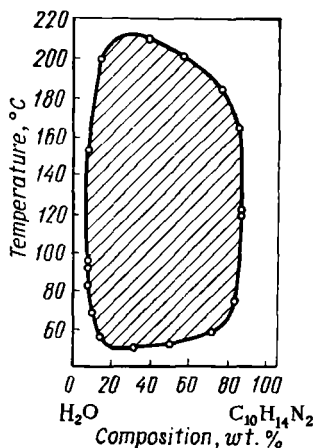


Fig. 1.6. Mutual solubility of water and nicotine

**The Solubility of Solids in Liquids.** The solubility of solid substances in water varies within wide limits. In most cases solubility increases with temperature. But there are exceptions to this rule. For example, gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , loses up to 75 per cent of its water of crystallization on heating and its solubility decreases. At a temperature of about  $200^\circ\text{C}$  hemihydrate gypsum becomes practically insoluble in water. This explains why it precipitates as scales on the walls of heat exchangers at high temperatures. The solubility of calcium oxide,  $\text{CaO}$ , lithium carbonate,  $\text{Li}_2\text{CO}_3$ , and of some other substances also decreases with increasing temperature.

The dissolution of a solid can be accelerated by reducing the particle size of the solute and thoroughly mixing with the solvent. This ensures a better contact of the solute with the solvent to accelerate the process of dissolution.

The dependence of the solubility of solids on temperature\* is expressed graphically by the *solubility curve* (Fig. 1.7). The study of solubility curves helps determine whether or not the composition of compounds formed by the solute with the solvent change. If the qualitative composition of the solute does not change with temperature, the solubility curve is regular. Abrupt changes or "breaks"

\* Schröder's equation describes the dependence of the solubility of solids in liquids on temperature:

$$\ln N = \frac{\Delta H_m}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right)$$

where  $\Delta H_m$  is the molar heat of melting of solute;  $N$  is solubility of the solute at a given temperature  $T$ ;  $T_m$  is the melting point of the solute, K; and  $R$  is the universal gas constant.

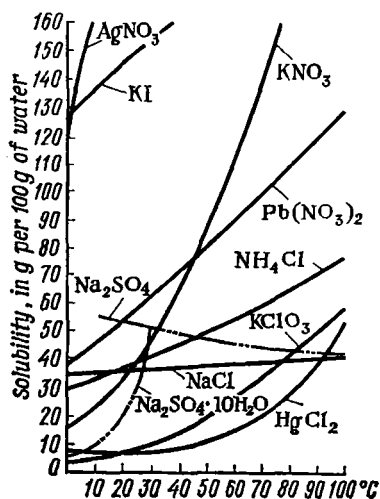


Fig. 1.7. Solubility curves

in the character of the curves indicate a change in the composition of the solute particles in solution. For example, the solubility of sodium sulphate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , increases with temperature from 0 to 32.28°C. The salt loses its water at temperatures above this point, and the solubility of anhydrous sodium sulphate decreases with further rises in temperature.

A measure of solubility of a substance in given conditions is the concentration of its saturated solution. *Solubility is the quantity, in grams, of solute which saturates 100 g of solvent in given conditions.*

A *saturated solution* is one in dynamic equilibrium with excess solute, i.e. the amount of solute which is crystallized out from the solution per unit time is equal to the amount of solute which passes into solution. Hence, the concentration of solute in a saturated solution remains constant.

Saturated solutions should be differentiated from concentrated solutions. A *concentrated solution* is a solution in which the concentration of solute is high. Saturated solutions of various substances differ greatly in their concentration. Saturated solutions of readily soluble substances have high concentration of solute while the concentration of saturated solutions of sparingly soluble substances is low.

If the concentration of a solution is lower than that of saturation in given conditions, the solution is said to be *unsaturated*. If the concentration of a solution is higher than the concentration of saturation, the solution is *supersaturated*. Supersaturated solutions are quite unstable. Excess solute can crystallize out on shaking or on addition of salt crystals or dust, these acting as centres of crystallization.

**Expressing Concentration.** Concentration is often expressed in percentage. The numerical value expressing the per cent concentration of solute in solution indicates the number of grams of solute contained in 100 g of solution.

A *molar*, or  $1M$ , solution is one containing a gram-molecule (mole) of solute in 1 litre of solution. Hence, *molarity is the concentration of a solution expressed by the number of moles of solute per litre of solution.*

A *molar* solution is one containing 1 mole of solute in 1000 g of solvent.

A *normal*, or *1N*, solution is a solution one litre of which contains 1 gram-equivalent of solute.

*Normality is the concentration of a solution expressed as the number of gram-equivalents of solute in 1 litre of solution.*

The *mole fraction*  $N_i$  of component  $i$  is the ratio of the number of moles  $n_i$  of this component to the total number of moles ( $n_1 + n_2 + n_3 + \dots + n_i$ ) and is determined by the formula

$$N_i = \frac{n_i}{n_1 + n_2 + n_3 + \dots + n_i}$$

---

## 1.3. General Properties of Solutions

The process of the formation of solutions does not only consist in physical processes involving the distribution of solute molecules between the molecules of solvent, but involves also chemical processes.

The molecules of solute react with the solvent to form complex compounds known as *solvates* (from the Latin *solvere*, to dissolve). If the solvent is water, these compounds are called *hydrates*. Solvates of many substances have been isolated from solution in the solid state. The fact that these compounds exist in solution is proved by the change in the heat of solution, sometimes the change in the volume of the solution, and even in its colour.

The heats of solution for many different substances have been studied. The amount of heat which is absorbed (or liberated) during dissolution of one mole of solute is known as the *heat of solution* of this substance.

When a solid is dissolved its crystalline lattice is destroyed and solvates are formed. The former process occurs with the absorption of energy and the latter with the release of energy. The final result arrived at for the heat of solution is equal to the sum of these heat effects. The result can be positive or negative. For example, during dissolution of one mole of ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , 6.4 kcal are absorbed, and during dissolution of one mole of potassium hydroxide,  $\text{KOH}$ , 12.8 kcal of heat are liberated.

Hence, solvent molecules in solution are bound in complexes with the solute and the concentration of free molecules of the solvent in it is lower than in pure solvent.

**Osmosis.** The decreasing number of free molecules of solvent in solution accounts for the phenomenon known as *osmosis* and for the decreased vapour pressure of the solvent vapour over the solution (with respect to pure solvent).

Osmosis occurs during the contact of two solutions of different concentrations separated by a semipermeable membrane which

passes the molecules of the solvent but prevents the passage of the molecules of the solute. Free molecules of the solvent pass into the more concentrated solution to further increase its concentration in it.

Hence osmosis occurs due to the tendency of solvent molecules to equilibrate the concentration on each side of the membrane. Osmosis is characterized quantitatively by *osmotic pressure*, which is equal to the external hydrostatic pressure that has to be applied to the system in order to stop osmosis.

The quantitative aspect of osmotic pressure was studied by the Dutch scientist van't Hoff (1852-1911), who established that osmotic pressure in solution depends on the quantity of solute particles contained in it (i.e. on the molal concentration). Solutions of equal molal concentrations must, at equal temperatures, have the same osmotic pressure. These solutions are called *isotonic*.

As van't Hoff studied osmotic pressure of different solutions he arrived at a conclusion that solute behaves like a gas: it tends to occupy the entire volume of the solvent like gas in a vessel.

So van't Hoff proposed using the equation for an ideal gas for the determination of osmotic pressure

$$pv = nRT$$

Substituting the number of moles of solute for its concentration  $c = \frac{n}{v}$  and substituting  $\pi$  for  $p$  we obtain

$$\pi = cRT$$

where  $\pi$  is osmotic pressure, atm;  $R$  is the gas constant, litre  $\times$  atm/deg  $\times$  mole;  $T$  is absolute temperature;  $c$  is molar concentration.

According to this equation, a unimolal solution of an undissociating solution, at 0°C, has an osmotic pressure 22.4 atm ( $\pi = 1 \times 0.082 \times 273 = 22.4$ ).

**Van't Hoff's Law:** *all dilute solutions are characterized by osmotic pressure equal to the gas pressure which the solute would exert if it existed as a gas and would occupy the same volume as that of the solution.*

Osmosis is a very important phenomenon in life. Most animal tissues are semipermeable. The processes of food assimilation and metabolism are closely connected with different permeabilities of tissues for water and dissolved substances. Osmosis accounts for the fact that fresh-water bacteria and fish cannot live in sea water and vice versa.

Osmosis is used in the purification of water by electrolysis with ionite membranes.

**Vapour Pressure of Solution.** Any liquid is found inequilibrium with its vapour. This means that the number of particles leaving

the solution per unit time is equal to the number of particles which return into the solution. The vapour pressure over pure solvent at which this equilibrium is attained is higher than over solution. This is because the solvent molecules are kept in solution by the solute. Hence, the lowering of vapour pressure over solution (with respect to that over pure solvent) is explained by the decreased number of free solvent molecules contained in it.

The quantitative characteristics of this lowering was established by the French scientist Raoult. Its law is formulated as follows: *the relative lowering of saturated vapour pressure of the solvent over dilute solutions of nonelectrolytes at constant temperature is equal to the mole fraction of the solute in the solution:*

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{n}{n + N}$$

where  $p_A^0$  is the saturated vapour pressure over pure solvent;  $p_A$  is the saturated vapour pressure of the solvent over the solution;  $(p_A^0 - p_A)$  is the lowering of the saturated vapour pressure over the solution, while  $\frac{p_A^0 - p_A}{p_A^0}$  is the relative lowering of the saturated vapour pressure;  $n$  is the number of moles of the solute; and  $N$  is the number of moles of the solvent.

All solutions boil at higher and freeze at lower temperatures than the pure solvent. This is explained by the lowered vapour pressure of solution compared with the vapour pressure of the pure solvent. A liquid starts boiling when the pressure of its vapour saturating the space above the solution is equal to the external pressure. A liquid freezes when the vapour pressure over the solid substance is equal to that over the liquid.

Consider curves describing vapour pressure changes associated with variations of temperature.

Figure 1.8 shows a curve  $OA$  which illustrates the vapour pressure over a pure solvent, and a curve  $O'A'$  of the pressure over the solution.

The vapour pressure over the solution is always lower than over the pure solvent, and therefore, to attain equilibrium with the external pressure, the solution should be heated over  $T_b$  of the pure solvent ( $T_b + \Delta T_b$ ) and cooled to the temperature below  $T_f$  of the pure solvent ( $T_f - \Delta T_f$ ). ( $T_b$  is the boiling point and  $T_f$  is the freezing point of the solvent.)

Experiments show that the elevation of the boiling point and the depression of the freezing point of a solution is proportional to the concentration of the solute:  $\Delta T_f = K_{cf}c$  where  $\Delta T_f$  is the depression of the freezing point of the solution with respect to pure solvent;  $c$  is the molal concentration of the solution (1 mole in 1000 g of solvent);  $K_{cf}$  is the cryoscopic constant. Or,  $\Delta T_b = K_{eb}c$ , where  $K_e$

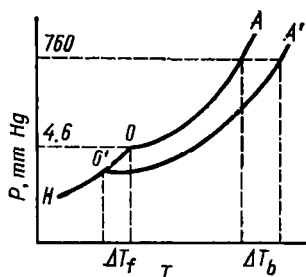


Fig. 1.8. Vapour pressure over pure water and solutions of nonvolatile substances

is the ebullioscopic constant;  $\Delta T_b$  is the elevation of the boiling point of the solution with respect to that of the pure solvent; and  $c$  is the molal concentration.

A unimolal aqueous solution of a nonelectrolyte freezes at a temperature  $1.86^\circ\text{C}$  below and boils at a temperature  $0.52^\circ\text{C}$  higher than pure water. These magnitudes are cryoscopic (Greek, *kryos*, cold) and ebullioscopic (Latin, *ebullire*, to boil out) constants. Ebullioscopic and cryoscopic constants depend on the nature of the solvent and do not depend on the nature of the solute.

Hence, the general properties of solutions show in osmosis, in the lowering of the vapour pressure of solutions, and the depression of the freezing point and elevation of the boiling point of solutions. All these properties of solutions obey one law, viz. the Raoult-van't Hoff law, which reads: *the properties of dilute solutions of nonelectrolytes are directly proportional to the number of solute particles, i.e. to the molal or molar concentration of the solute.*

**The Special Properties of Electrolyte Solutions.** The equations describing the general properties of nonelectrolyte solutions can be applied to solutions of electrolyte, provided a correction is introduced. The latter was proposed by van't Hoff and is known as the *isotonic coefficient*. The isotonic coefficient  $i$  indicates how much the number of dissolved particles in an electrolyte solution exceeds the number of particles in an equimolecular solution of a nonelectrolyte. This value can be determined by any of the following ratios:

$$i = \frac{\Delta t'_f}{\Delta t_f} = \frac{\Delta t'_b}{\Delta t_b} = \frac{\pi'}{\pi} = \frac{\Delta p'}{\Delta p}$$

where the numerator is the value obtained for a solution of an electrolyte experimentally, while the denominator is the value calculated for the corresponding solution of a nonelectrolyte of the same concentration. For example, for osmotic pressure of an electrolyte solution, the formula  $\pi = iCRT$  should be used. The isotonic coefficient for electrolytes is always greater than unity.

## 1.4. Fractional Distillation

The boiling point of solutions consisting of two volatile substances can be found from the diagram shown in Fig. 1.9. In this case the composition of the vapour differs from the composition of the liquid and is characterized by the first law of Kononov (1881): *a saturated*

vapour, compared with an equilibrium solution, is relatively richer in the component whose addition to the system increases the total vapour pressure. Figure 1.9 shows the isobaric diagram of the dependence of the boiling point of a solution on the composition of the liquid phase (lower curve) and the vapour condensation temperature on the composition of the vapour phase (upper curve). The upper field on the diagram  $t_b - x$  corresponds to vapour and the lower to liquid. The difference in the composition of the liquid and gaseous phases is widely used in the practical fractionation of liquid mixtures.

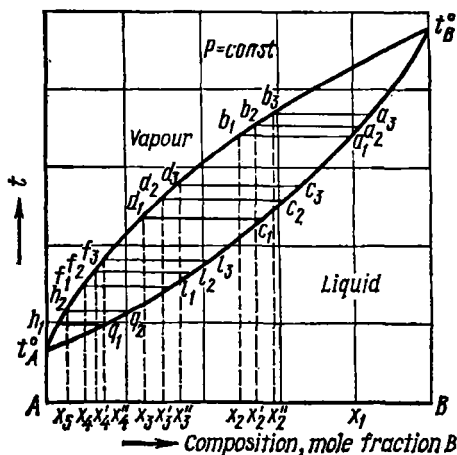


Fig. 1.9. Boiling point versus composition of a binary system

If an initial mixture of composition  $x_1$  is heated to boiling point (at  $p = \text{const}$ , point  $a_1$ ) the first portions of vapour (point  $b_1$ ) have the composition  $x_2$ . During the evaporation process, the composition of the liquid and of vapour changes (points  $a_2$  and  $b_2$  respectively). The condensation of this vapour gives the first liquid fraction with composition  $x'_2$ . Further evaporation of the liquid with subsequent condensation gives liquid fractions having the compositions  $x'_2, x''_2$ , etc.

If we heat a condensed fraction, e.g.  $x'_2$ , to boiling at point  $c_1$ , we have the first portions of vapour corresponding to point  $d_1$  (composition  $x_3$ ). Next we obtain the first fraction of condensate having the composition  $x'_3$ , and so on until we obtain pure component B, i.e. the content of the component B in the fractions varies from  $x'_3$  to 1.

If we repeat the same operations, beginning with the fraction of the composition  $x'_3$ , and then  $x''_3$ , we obtain a series of portions of vapour corresponding to points  $f_1, f_2, \dots, n_1, n_2$  and a series of the corresponding condensate fractions. If now we put together the fractions of about the same composition and repeat the fractionation process, we obtain pure components A and B.

In distillation columns provided with partial condensers and also in rectification columns, the subsequent distillation steps are unified in a single automated process by which liquid solutions are separated (rectification). If the composition of the liquid and vapour phases is similar, both curves on the diagram  $t_b - x$  meet at the maximum (Fig. 1.10) or the minimum (Fig. 1.11) at certain concentra-

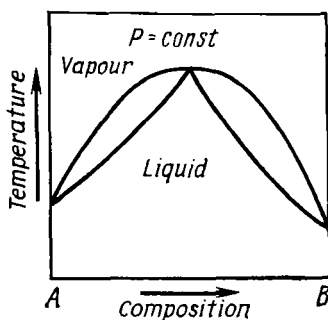


Fig. 1.10. Dependence of the boiling point on the composition (an azeotropic mixture)

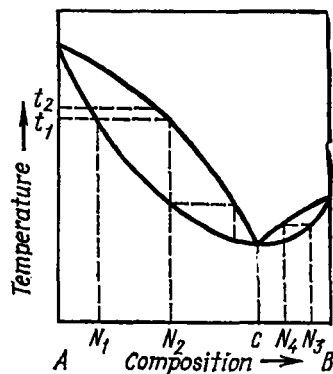


Fig. 1.11. Dependence of the boiling point on the composition of a system (with the azeotropic point)

tions of the solute. Such mixtures do not change their composition during boiling and are known as *azeotropic (constant boiling) solutions*. For example: (a) 95.57 per cent ethyl alcohol; (b) 20.3 per cent hydrochloric acid; (c) 68 per cent nitric acid. All these substances form azeotropic mixtures with water.

## CHAPTER TWO

# KINETICS OF CHEMICAL REACTIONS

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## 2.1. Factors Affecting the Rate of Chemical Reaction

Kinetics of chemical reactions is a branch of science dealing with the rates of chemical reactions and their dependence on various factors.

In order to make practical use of any reaction it is necessary to know the rate at which it proceeds. The productivity of chemical equipment and hence the amount of chemical products obtained on this equipment often depends on the rate of the reactions involved.

The prerequisite condition for a chemical reaction is the collision of the molecules of the reactants. The molecules must first approach each other to the point at which the electric fields excited by their electrons overlap. It is only under these conditions that the electron clouds can be displaced and the atoms rearranged to form new molecules. But it is not any molecular collision that can produce a chemical reaction. A chemical process is caused by the collision of molecules having high energies, i.e. active molecules.

The energy required to activate the initial particles is known as the *activation energy* of a reaction. In some cases the activation energy is the main factor determining the rate of a chemical process. The higher the energy, the less the number of molecules possessing this energy at a given temperature and the slower the chemical reaction. It has been established practically that processes with activation energies less than 10 kcal/mole proceed at a high rate at normal temperature, while the rate is immeasurably low at activation energies over 30 kcal/mole.

The rate of a chemical reaction depends on the nature of the reactants and also on the conditions under which the reaction proceeds.

The main conditions affecting the rate of a chemical reaction are as follows: (1) the concentration of the reacting substances; (2) temperature; (3) the presence of a catalyst, etc.

**Effect of Concentration.** The effect of concentration of the reactants on the rate of a chemical reaction is expressed by the Guldberg-Waage law, also known as the *law of mass action*.

If substances A and B react to give the product AB the reaction can be expressed as



According to the aforementioned law, the rate of this reaction is

$$v = k [A] [B]$$

where  $k$  is a proportionality constant, also called the *velocity* or *rate constant*;  $[A]$  and  $[B]$  are the molar concentrations of substances A and B involved in the reaction.

The velocity constant  $k$  has a certain physical sense. It is equal to the rate of a chemical reaction when the concentration of each reactant is unimolar, i.e. 1 mole/litre, or when the product of their concentrations is equal to unity.

In a more general form, when the numerical coefficients in the reaction equation are not unity, as for example in the following equation



the reaction rate has the following mathematical expression

$$v = k [A]^m [B]^n$$

i.e. *the rate of a chemical reaction at constant temperature is proportional to the product of the concentrations of the reactants raised to the power of their stoichiometric coefficients\**.

**Effect of Temperature.** The velocity of motion of molecules increases with temperature and they collide at a higher frequency. This is one of the causes by which the reaction rate increases with rising temperature. Another cause is that molecules become more active at high temperatures, and the number of effective collisions thus increases.

To accelerate a chemical reaction, the system is often heated. Experience shows that when temperature increases  $10^\circ\text{C}$ , the reaction rate increases approximately 2-3 times (van't Hoff's rule).

The ratio of the velocity constants for two different temperatures ( $t$  and  $t + 10^\circ\text{C}$ ) is called the *temperature coefficient* of a chemical reaction rate and is designated by  $\gamma_t$ .

The mathematical expression of the dependence of reaction rate on temperature is

$$v_{t_2} = v_{t_1} \gamma^{\frac{t_2 - t_1}{10}}$$

where  $v_{t_1}$  is the initial reaction rate at temperature  $t_1$ ;  $v_{t_2}$  is the reaction rate after a rise in temperature to  $t_2$ ;  $\gamma$  is the temperature coefficient of the reaction, i.e. the value showing how much the reaction rate increases with a rise in the temperature of the reactants by  $10^\circ\text{C}$ .

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\* The basic law of kinetics is applicable only to liquid and gaseous systems; solid systems do not obey this law.

**Example.** The temperature coefficient of the reaction  $\gamma = 2$ . Calculate in what time the reaction will be accomplished at  $100^\circ\text{C}$  if at  $0^\circ\text{C}$  it is accomplished in ten minutes.

**Solution.** The reaction rate is inversely proportional to time  $\tau$  required to accomplish it, i.e.  $\frac{v_{t_2}}{v_{t_1}} = \frac{\tau_1}{\tau_2}$ . Substitute the value  $v_{t_2} = v_{t_1} \gamma^{\frac{t_2 - t_1}{10}}$  into the formula to find

$$\frac{v_{t_1} \gamma^{\frac{t_2 - t_1}{10}}}{v_{t_1}} = \frac{\tau_1}{\tau_2}, \quad \text{whence} \quad \tau_2 = \frac{\tau_1}{\gamma^{\frac{t_2 - t_1}{10}}} = \frac{10 \times 60}{2^{10}} = 0.6 \text{ sec}$$

The van't Hoff temperature coefficient ( $\gamma$ ) can be used only for tentative calculations within a small range of temperatures because the coefficient itself slightly changes with temperature.

A more accurate dependence of the velocity constant on temperature is described by the Arrhenius equation obtained by formal analysis of the van't Hoff isochore equation. This equation has the form  $\frac{d \ln k}{dT} = \frac{E}{RT^2}$  where  $k$  is the velocity constant,  $T$  is temperature in K,  $R$  is the universal gas constant, and  $E$  is the energy of activation.

*Activation energy is the minimum excess energy, compared with the mean energy of the reacting molecules at a given temperature, which the molecules need to possess if their collision is to produce a new product.*

The integration of the Arrhenius equation gives the following:  $\ln k = -\frac{E}{RT} + \ln C$ , where  $\ln C$  is the integration constant.

The magnitude  $\ln C$  can be determined graphically from the dependence of the logarithm of the velocity constant on the reciprocal value of absolute temperature. If this dependence is expressed by a line inclined to the X-axis (Fig. 2.1), then  $\ln C$  is equal to the y-intercept at  $\frac{1}{T} = 0$ . The slope of the straight line  $\phi$  is used to determine the ratio of the activation energy to the gas constant:  $\tan \phi = -\frac{E}{R}$ . Whence the magnitude of the energy of activation of a chemical reaction can be found.

The activation energy can also be determined from experimental data obtained for two values of velocity constants at two different temperatures. To that end, the Arrhenius equation  $\frac{d \ln k}{dT} = \frac{E}{RT^2}$  is integrated from  $T_1$  to  $T_2$  to obtain the following expression:

$$\ln \frac{k_2}{k_1} = \frac{E}{R} \frac{T_2 - T_1}{T_1 T_2}$$

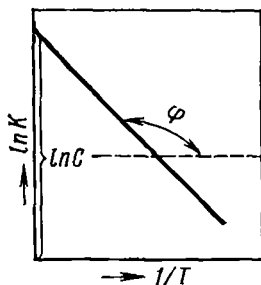


Fig. 2.1. Dependence of the logarithm of the reaction velocity constant on the inverse temperature ( $1/T$ )

where  $k_2$  is the velocity constant of a chemical reaction at temperature  $T_2$ , and  $k_1$  is the same at temperature  $T_1$ .

If the activation energy of a given reaction is known, this equation can be used to determine the velocity constant of the reaction at any other temperature.

The exponential form of the Arrhenius

equation is  $k = Ce^{-\frac{E}{RT}}$ , where  $C$  is the *pre-exponential* (or the *frequency*) factor.

According to the theory of collisions, the factor  $C$  has the sense of the total number of collisions of molecules per second inside a volume of one cubic centimetre. It is measured on the basis of molecular-kinetic

theory. But this calculation gives exaggerated values for reaction rates in solution, and in order to reconcile them with experience an additional factor, the spatial or probability factor  $P$ , is introduced into the equation. (The value of  $P$  depends on the nature of the reactants and can vary from 1 to  $1 \times 10^{-8}$ . This factor takes into account the position of the reacting particles at the moment of collision and the duration of contact necessary for the redistribution of energies inside these molecules by their bonds. It shows that even a collision of active molecules does not always result in completion of a chemical process.)

This equation shows that the constants characterizing the reaction are the pre-exponential factor  $C$  and the activation energy  $E$ . The higher is  $E$ , the lower (at a given  $C$ ) the rate of a chemical reaction.

**Effect of Catalysts.** Catalysts are substances which alter the rate of the reaction. Although they are directly involved in the reaction, they remain unchanged in quality and quantity. Catalytic processes occur widely in nature. For example, water is a universal catalyst. In the total absence of water, chlorine does not act on metals; hydrofluoric acid does not destroy glass; sodium and phosphorus are not oxidized in air, and oxyhydrogen gas does not explode even at  $1000^\circ\text{C}$ . In some cases reactions proceed at different rates depending on the nature of the material of the reactor, which can act as a catalyst. For example, the reaction  $\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}$  occurs in a glass vessel in the form of an explosion even at the temperature of liquid air. The same reaction in a silver vessel occurs only under normal conditions, and in a magnesium vessel only with heating.

Biological catalysts are important for vital processes in nature. These are enzymes, complicated organic substances of a protein nature, formed in animal and plant organisms.

**Catalytic Processes.** Most chemical reactions pass through an active complex whose composition, structure and properties determine the kinetic properties of the system, viz., the reaction rate, its direction, the effect of the external factors, etc.

The process by which is formed an active complex comprising a substance which is not stoichiometrically involved in the overall process but changes the kinetic properties of the system is called *catalysis*, while the substance which changes the rate of the reaction and recovers its chemical properties is called the *catalyst*.

Homogeneous and heterogeneous catalyses are distinguished. If a catalyst and the reactants exist in one phase, the catalyst is called *homogeneous*; and if in different phases, *heterogeneous*. There exists a phenomenon known as *autocatalysis*; the catalyst here is formed in the course of the reaction. For example, as ferrous oxide is reduced with hydrogen, iron produced by the reaction  $\text{FeO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{Fe}$  acts as a catalyst. The rate  $v$  of autocatalytic processes is a function of time  $\tau$ ;  $v = \varphi(\tau)$  (Fig. 2.2). For some values of  $\tau_2$ , the rate peaks and then decreases. This is explained by the fact that at the beginning of the process the catalyst is present in insufficient amounts, but as the peak is attained the concentration of the initial reactants decreases. Autocatalytic processes occur in the purification of natural water, for example, during the removal of iron by filtering water through sand coated in iron hydroxide.

**The Special Properties of Catalysts.** 1. Catalysts change the rate of only those reactions which are realizable thermodynamically in given conditions.

2. Catalysts do not shift chemical equilibrium in reversible processes but only help attain equilibrium.

3. Catalysts do not change the thermodynamic characteristics of reactions ( $\Delta H$ , change of enthalpy;  $\Delta U$ , change in the internal energy;  $\Delta G$ , change in free energy, etc.) but affect the kinetic characteristics, viz., activation energy  $E$ , pre-exponential factor  $C$  from the Arrhenius equation.

4. Catalysts take an active part in chemical processes to form intermediate compounds or to break bonds between atoms in the molecule. These processes decrease the energy of activation of the system to accelerate the chemical process. If we assume that for reactions in the gaseous phase, other things being equal, the pre-exponential factors of catalyzed and uncatalyzed processes are close in magnitude, then the rate of a catalyzed reaction  $v_{\text{cat}}$  is

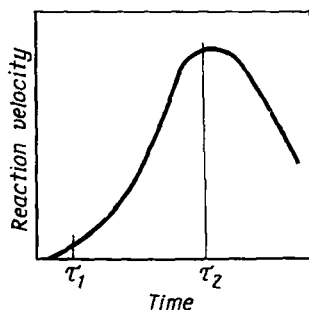


Fig. 2.2. Variation of the velocity of an autocatalytic reaction with time at constant temperature

greater than the rate of an uncatalyzed reaction  $v_{\text{uncat}} e^{\frac{\Delta E}{RT}}$  times or  $\frac{v_{\text{cat}}}{v_{\text{uncat}}} = e^{\frac{\Delta E}{RT}}$ , where  $\Delta E$  is the difference in the activation energies of an uncatalyzed reaction  $E_1$  and a catalytic reaction  $E_2$ ; ( $\Delta E = E_1 - E_2$ ).

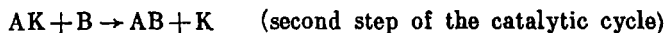
5. Catalysts do not change the heat effect of the reaction.

6. Catalysts act selectively. This indicates that a catalyst affects the rate of only one or a few reactions. If given substances can react by different thermochemical pathways, one catalyst can change the rate of the reaction proceeding by one mechanism, with another catalyst affecting the other mechanism. For example, ethyl alcohol can be processed into various products depending on the particular catalyst used in the reaction. If a copper catalyst is used, and the reaction is effected at a temperature of 473-523 K, acetaldehyde is

produced:  $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array} + \text{H}_2$ ; the reaction at a temperature of 623-633 K in the presence of  $\text{Al}_2\text{O}_3$  or  $\text{ThO}_2$  gives ethylene:  $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ .

**Homogeneous Catalyst.** In the field of homogeneous catalysis, the theory of intermediate compounds proposed by Paul Sabatier and developed by N. D. Zelinsky and his pupils prevails.

The main postulates of the theory are as follows: (1) a catalyst takes an active part in the chemical process to form an unstable active complex (intermediate compound) which then turns into the reaction product with the regeneration of the catalyst; (2) the chemical interaction of the catalyst with the initial substances changes the thermochemical path of the reaction to decrease the activation energy of the system (positive catalysis). In the general form this process can be represented as follows: substances A and B react with a catalyst K. One of the reactants forms an intermediate compound with the catalyst:



Hydrogen ions and hydroxyl ions have a significant effect on the rate of homogeneous reactions in the liquid phase (acid-base catalysis). If only one acid or one alkali are present in the solution, the velocity constant of the reaction occurring in it is directly proportional to the concentration of hydrogen or hydroxyl ions:  $K = K_{\text{H}^+} [\text{H}^+]$ ;  $K = K_{\text{OH}^-} [\text{OH}^-]$ , where  $K_{\text{H}^+}$  and  $K_{\text{OH}^-}$  are catalytic constants of hydrogen and hydroxyl ions. The ionic mechanism of the catalytic action is most probable in these cases.

The effect of the ionic strength on the velocity constant of the reaction in the homogeneous system can be expressed, for simple

cases, by the following equation:

$$\ln K = \ln K_0 + 1.02 z_A z_B \sqrt{I}$$

where  $K_0$  is the velocity constant for infinite dilution;  $I$  is the ionic strength of the solution ( $I = \frac{1}{2} \sum m z^2$ );  $z_A$  and  $z_B$  are charges on the reactant particles;  $m$  is the molar concentration of the electrolyte. Hence, the logarithm of the velocity constant for a chemical reaction is a linear function of the quadratic square of the ionic strength of the solution.

**Heterogeneous Catalysis.** Heterogeneous catalysis is often used to purify natural waters and effluents. The catalyst is in the solid phase, while the reactants are liquids or gases.

The catalyst must be active, stable up to high temperatures, and mechanically strong. These properties are given to the catalyst during its manufacture, and therefore catalysts are often not pure substances but complicated multicomponent systems. Three types of catalysts are known: *mixed*, *supported on carriers*, and *promoters*.

Mixed catalysts are usually mixtures of two or more oxides, e.g.:  $\text{Al}_2\text{O}_3 + \text{ThO}_2$ ;  $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ ;  $\text{CoO} + \text{MgO}$ . The activity of these catalysts is a function of their composition and catalysts having maximum activity can therefore be prepared by varying the proportion of the components in the system. The oxygen content in such catalysts is often less than in each separate component.

In order to reduce catalyst waste and to promote its activity and stability over temperature fluctuations, and to lessen catalyst poisoning, adsorbed (supported on a carrier) catalysts are often used. These are prepared by applying a thin layer of the catalyst to a porous or inactive material known as a carrier. Materials with a developed specific surface are used for the purpose. These are charcoal, alumogel, silica gel, pumice, talcum, asbestos, glass, porcelain, etc. More active catalysts are prepared on carriers which deform the structure of the catalyst atoms to a greater extent. The higher the charge and the lesser the ionic radii of the carrier material, the greater the deforming action it produces on the catalyst.

Promoters are obtained by applying substances which are noncatalytic but only increase the activity of a given catalyst (by increasing the number of active centres on the material). Two types of promoting action are distinguished: structure forming promotion and modification. The catalysts assigned to the former group stabilize the active phase of the catalyst (for example, they make them less vulnerable to the action of heat or poisons). This increases their life and service. The modifying of catalysts consists in changing the structure and chemical composition of their active phases. Active centres of a new chemical nature are synthesised on the catalyst surface, by which even the selectivity of the catalyst can be modified.

Any heterogeneous catalytic reaction begins with the adsorption of molecules of the initial reactants on the surface of a solid catalyst. Heterogeneous catalysis can be divided into three stages: (1) movement of the reactants toward the surface of the catalyst (diffusion); (2) reaction on the catalyst surface, and (3) desorption of the reaction products from the catalyst with recovery of its surface. The rate of a catalytic process depends on any of these three stages.

The first stage in heterogeneous catalysis obeys the first order equation for the concentration in a volume of solution ( $c_s$ ):

$$\frac{dc}{d\tau} = \frac{D\sigma}{v\delta} (c_s - c_x)$$

where  $D$  is the diffusion coefficient;  $\sigma$  is the surface;  $c_x$  is the concentration of the reactants at the catalyst;  $v$  is the volume;  $\delta$  is the distance from the catalyst.

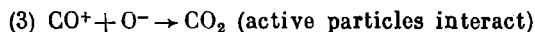
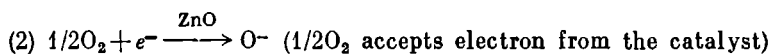
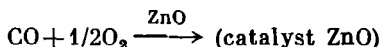
The rate of the diffusion process increases with rising temperature according to a law similar to the Arrhenius equation:  $D = ke^{-\frac{E}{RT}}$ , but this increase is smaller than in chemical processes.

The reaction is effective only on the active parts of the catalyst surface and only reversible activated adsorption causes a reaction in the surface layer of the catalyst. Physical adsorption has no direct connection with catalysis, because the molecular structure remains unchanged in this process. In reversible activated adsorption, the bonds between atoms in molecules of the initial substance are loosened and the molecules are activated.

Desorption of the reaction products must be spontaneous and fast because an irreversible activated adsorption blocks the catalyst surface.

**Selection of a Catalyst.** The selection of a catalyst depends on the character of the reaction. If the reaction involves electron transfer (oxidation-reduction reactions) its kinetic characteristics will be changed by catalysts with free electrons. These are  $d$ -electron metals and their oxides. Semiconductors can act like catalysts. The higher the electric conductivity of the conductor, the better its catalytic properties.

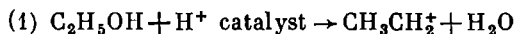
The mechanism of catalytic processes consists of the transfer of electrons from the reacting molecules to the catalyst and back. For example,



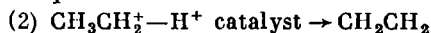
Exchange reactions, not connected with electron transfer, can be catalyzed by substances containing mobile hydrogen ions or hydroxyl ions (acid-base catalysis). These are hydroxides of iron, aluminium, zirconium, thorium, and of other metals.

The activity of an acid catalyst depends on the amount of mobile hydrogen capable of transfer from the catalyst to the reactant molecules.

The hydrogen mobility is high in mixed catalysts such as aluminosilicates and zirconium silicates (their acidity is close to that of  $\text{H}_2\text{SO}_4$ ). Consider the dehydration of ethyl alcohol:



A carbonium ion is formed in the reaction. It is destroyed on the surface of the catalyst to liberate a molecule of an unsaturated hydrocarbon and a proton is returned to the catalyst:



Hence the mechanism of proton catalysis consists of the continuous transition of protons from the catalyst to the reacting molecules and back.

## 2.2. Order of Reaction

The methods of chemical kinetics, which determine the order of the reaction, are often used to assess regularities in the processes occurring in the purification of natural waters and effluents.

*The order of a chemical reaction with respect to a given substance is the number equal to the power to which the concentration of this substance is raised in the kinetic equation  $v = Kc_A^{n_1}c_B^{n_2}$ . The sum of the exponents ( $n_1 + n_2 + n_3 + \dots$ ) of concentrations of all initial substances in the kinetic equation determine the order of the reaction on the whole.*

$v_1 = Kc_A^0$  is the equation of the reaction of zero order. The kinetic equation of zero order can be described by the equation:

$$K = \frac{c^0 - c}{\tau}$$

where  $K$  is the velocity constant of a chemical reaction;  $c^0$  is the initial concentration of the reactants;  $c$  is the concentration of the substance at time  $\tau$ . Zero order reactions are possible, provided the concentrations of the initial substances are constant. Zero order reactions occur mainly in heterogeneous systems where the consumed reactant is supplied from the other phase.

$v_2 = K_2c_A$  is the equation of the first order reaction;  $v_3 = K_3c_A^2$ , second order reaction .... The kinetic equation of the first order

reaction establishes the rate at which the initial substances are converted over time:

$$K = \frac{1}{\tau} \ln \frac{a}{a-x}$$

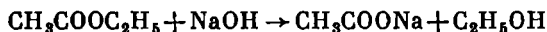
where  $K$  is the velocity constant of a chemical process;  $a$  is the initial concentration of the reactant, mole/litre;  $x$  is the concentration of the reacted substance at time  $\tau$ , mole/litre;  $(a - x)$  is the remaining equilibrium concentration at time  $\tau$ , mole/litre.

Chemical processes in which one of the reactants changes its concentration, while the concentration of the second reactant because of its high concentration changes insignificantly, are first order reactions (hydrolysis of salts).

The kinetic equation of the second order reaction has the following form

$$K = \frac{1}{\tau} \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

where  $a$  is the initial concentration of substance A, mole/litre;  $b$  is the initial concentration of substance B, mole/litre;  $(a - x)$  is the equilibrium concentration of substance A at time  $\tau$ , mole/litre;  $(b - x)$  is the equilibrium concentration of substance B at time  $\tau$ , mole/litre. The reaction of the saponification of an ester with an alkali is second order:



It follows, therefore, that the order of the reaction characterizes the formal-kinetic dependence of the reaction rate on the concentration of the reactants, while molecularity characterizes the elementary mechanism of each separate step of the complicated process. It is obvious that the molecularity of the reaction coincides with reaction order only in simple reactions.

**Determining Reaction Order.** The order of the reaction is determined experimentally by measuring the change in the concentration over time when there is a great excess of one of the components, and then with an excess of the other reactant. The change in the concentration of the reactant taken in excess is disregarded and the stoichiometric coefficient of the reactant taken in the low concentration is determined.

Consider the following case. The reactants  $aA + bB \rightarrow$ ; the rate of the reaction  $v = Kc_A^a c_B^b$ . The overall order of the reaction is determined by the sum  $(a + b)$ . Particular orders of reactions are determined by either of the following methods.

1. The method of trial involves substituting concentrations of each reactant found experimentally for each moment from the beginning of the reaction in the kinetic equations of reactions of various orders.

The order of the reaction corresponds to that kinetic equation for which the velocity constants remain constant at various initial concentrations of the reactants and at various intervals of time at a given temperature.

2. Graphical methods: (a) a function of concentration is found which, when plotted against time, gives a straight line on a graph. If such a function is  $\ln c$ , this is a first order reaction; if  $\frac{1}{c}$ , the reaction is second

order, if  $\frac{1}{c^2}$ , third order (Fig. 2.3); (b) use is made of the dependence of the reaction rate on the concentration  $v = kc^n$ . By taking logarithms  $\ln v = \ln k + n \ln c$ ;  $\tan \varphi = n$  (Fig. 2.4).

The rate of the reaction at any given moment of time can be determined by the slope of the tangent to the curve  $c = f(\tau)$  at the point corresponding to the relevant period of time from the beginning of the reaction (Fig. 2.5).

3. Using the half-life period during which the initial concentration of the reactant is halved:

(a) for first order reaction  $\tau_{1/2} = \frac{0.693}{k}$

(b) for second order reaction  $\tau_{1/2} = \frac{1}{kc_0}$

(c) for third order reaction  $\tau_{1/2} = \frac{3}{2kc_0^2}$

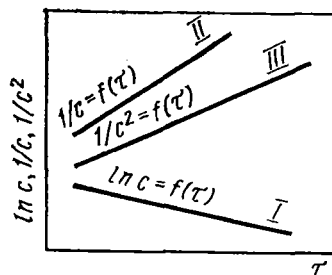


Fig. 2.3. Changes in the functions of the concentration of the initial substances with time in various orders of reactions

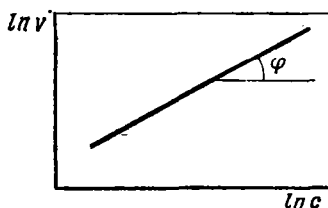


Fig. 2.4. Dependence of the logarithm of the reaction velocity on the logarithm of the concentration of the initial substances

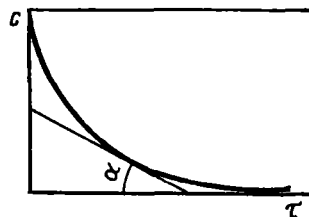


Fig. 2.5. Changes in the concentration of one of the initial substances over time

## 2.3. Thermodynamic Potentials of Chemical Reactions

Natural waters and effluents are treated by many chemical processes the direction of which can be predicted from the change in the thermodynamic potentials of the components involved. Most conve-

nient for this purpose are the Gibbs free energy ( $G$ ) and Helmholtz free energy ( $F$ ). The latter is used for the determination of the direction and the extent to which spontaneous processes can continue in a nonisolated system (at  $v$ ,  $T = \text{constant}$ ). The Gibbs free energy characterizes the same processes at constant pressure and temperature.

Thermodynamic potentials are thermodynamic functions which do not depend on the transition states of the processes but depend only on the initial and final states of the reactants.

The Gibbs free energy is equal to  $G = H - TS$ ; the Helmholtz free energy,  $F = U - TS$ , where  $H$  is the enthalpy (heat content of the system);  $U$  is the internal energy;  $T$  is the Kelvin temperature;  $S$  is the entropy\*, the function of the probability of the system (measure of the disorder of the system  $S = f(W)$ , or  $S = k \ln W$ , where  $k$  is the Boltzmann constant  $k = \frac{R}{N}$ ;  $W$  is the thermodynamic probability).

Absolute magnitudes of these values are difficult to determine but their change can be easily calculated from the mathematical equation of the first and the second laws of chemical thermodynamics,  $-\delta A' = TdS - dU - pdv$ , where  $\delta A'$  is nonmechanical work (against electric, magnetic, and other forces). Applying this equation to the isochoric ( $v$ ,  $T = \text{const}$ ) and isobaric ( $p$ ,  $T = \text{const}$ ) processes and integrating it within the limits of two states of the system, we obtain the following:

(a) for the isochoric process

$$A'_v = T(S_2 - S_1) - (U_2 - U_1) = (U_1 - TS_1) - (U_2 - TS_2) = -\Delta F$$

(b) for the isobaric process

$$\begin{aligned} A'_p &= T(S_2 - S_1) - (U_2 - U_1) - p(v_2 - v_1) = \\ &= (U_1 + pv_1 - TS_1) - (U_2 + pv_2 - TS_2) = \\ &= (H_1 - TS_1) - (H_2 - TS_2) = -\Delta G \end{aligned}$$

Quantities  $\Delta F$  and  $\Delta G$  characterize, respectively, free energy at constant volume and pressure; in a reversible isothermic process this energy can be converted into work.

The product of temperature and entropy ( $TS$ ) is *bound energy*. This is the energy which cannot be converted into work.

Hence, *the change in thermodynamic potentials is equal to maximum useful work taken with the sign reversed*. If  $\Delta F$  or  $\Delta G$  are zero, the system is at thermodynamic equilibrium. Only those processes in which  $\Delta F$  and/or  $\Delta G$  are less than zero can occur spontaneously.

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\* Growing entropy in an isolated system indicates the direction of the process.

So, the possibility, direction, and the limits of the *isobaric* or *isochore-isothermic processes* in a nonisolated system are determined by the sign of the difference  $\Delta G = G_2 - G_1$ , while the thermodynamic possibilities of the process by the absolute magnitude of the difference.

**Example 1.** Using the reaction described by the thermodynamic equation  $\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{O}_2(\text{g})$ , determine the direction of the reaction under standard conditions if the change in the Gibbs free energies of the formation of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_4$  are  $-394.92 \times 10^6$ ,  $-237.45 \times 10^6$ , and  $-50.85 \times 10^6 \text{ J} \times \text{kmole}^{-1}$ .\*.

**Solution.** The change in the thermodynamic potential of the reaction is equal to the sum of the changes in the potentials of the reaction products less the sum of the changes in the potentials of the starting reactants:

$$\begin{aligned}\Delta G &= \Delta G_{\text{CH}_4} - \Delta G_{\text{CO}_2} - 2\Delta G_{\text{H}_2\text{O}} = \\ &= [-50.85 - (-394.92) - 2(-237.45)] \times 10^6 = 818.97 \times 10^6\end{aligned}$$

The change in the Gibbs free energy of a chemical process indicates that, under standard conditions, only the reverse process is possible.

**Example 2.** Determine if water can be obtained from the reaction between hydrogen and oxygen under standard conditions if  $\Delta H$  of water formation is  $-286.15 \times 10^6 \text{ J} \times \text{kmole}^{-1}$  while the entropies of water, hydrogen and oxygen, under the same conditions, are 70,020, 130,730, and  $205,250 \text{ J} \times \text{deg}^{-1} \times \text{kmole}^{-1}$  respectively.

**Solution.** Determine the thermodynamic sum of the process' entropy

$$\begin{aligned}\Delta S_{298} &= S_2^0 - S_1^0 = S_{298(\text{H}_2\text{O})}^0 - S_{298(\text{H}_2)}^0 - \frac{1}{2} S_{298(\text{O}_2)}^0 = \\ &= 70,020 - 130,730 - \frac{1}{2} 205,250 = -163,345 \text{ J} \times \text{deg}^{-1} \times \text{kmole}^{-1}\end{aligned}$$

Using the equation  $\Delta G = \Delta H - T\Delta S = -286.15 \times 10^6 - 298(-163,345) = -237.45 \times 10^6 \text{ J} \times \text{kmole}^{-1}$ , we find the change in the thermodynamic potential.

The thermodynamic possibility of the formation of water from hydrogen and oxygen under standard conditions is very great ( $\Delta G \ll 0$ ), but the reaction does not occur because the system is at a false equilibrium due to the high kinetic resistance. If the activation energy of the system is lowered, for example by adding a catalyst, the reaction realizes its thermodynamic possibilities instantaneously (with an explosion).

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\* Values of free energy, entropy, and enthalpy can be found in chemical reference books.

## CHAPTER THREE

# CHEMICAL EQUILIBRIUM

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### 3.1. Equilibrium in Homogeneous Systems

A chemical reaction occurring within the limits of one phase is known as a *homogeneous chemical reaction* (for example, in solutions or in the gaseous phase). All chemical reactions are divided into *reversible* and *irreversible reactions*. Irreversible reactions proceed in one direction to full completion. At least one of the reactants is fully consumed in such processes. Reversible reactions are those in which the obtained products react again to form the initial substances. Hence reversible reactions proceed, in the same given conditions, simultaneously in two directions:  $A + B \rightleftharpoons C + D$ . A reversible reaction does not proceed to the end but only to a certain moment when the rates of both processes, viz. the forward and reverse processes, become equal, i.e. a dynamic equilibrium in the system is attained. As soon as this occurs, the concentrations of all reactants in the equilibrated system remain unchanged for an indefinitely long period of time.

Write down an equation for forward and reverse reaction velocities:

$$v_1 = k_1 [A] [B]; \quad v_2 = k_2 [C] [D]$$

where  $v_1$ ,  $k_1$  and  $v_2$ ,  $k_2$  are the reaction rates and velocity constants of the forward and reverse reactions respectively.

At chemical equilibrium, the rates of the forward and reverse reactions are equal, i.e.  $v_1 = v_2$ . Hence,  $k_1 [A] [B] = k_2 [C] [D]$ .

The conversion of the latter equation gives the following:

$$\frac{k_1}{k_2} = \frac{[C] [D]}{[A] [B]}$$

The ratio of the two constants  $k_1$  and  $k_2$  is also a constant, known as the *equilibrium constant*:

$$K = \frac{k_1}{k_2} = \frac{[C] [D]}{[A] [B]}$$

The mathematical representation of the equilibrium constant, when the reactants are taken in quantities of a few moles and react according to the equation  $aA + bB \rightleftharpoons cC + dD$  is, in the general

form, as follows:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The relationship between the concentrations of the reactants and the equilibrium constant is a mathematical expression of the law of mass action, and can be formulated as follows: *at a given temperature the ratio of the product of equilibrium concentrations of the reaction products to the product of equilibrium concentrations of the initial substances in a given reversible reaction is, in the state of chemical equilibrium, a constant value, the concentration of each reactant being raised to the power of its stoichiometric coefficient.*

The equilibrium constant has a definite physical sense. It is the ratio of the velocity constants of the forward and reverse reactions, this showing how much the rate of the forward reaction exceeds that of the reverse one at the same temperature and at a concentration of 1 mole/litre.

The equilibrium constant depends not on the concentration but on the nature of the reactants and the temperature. For a given reaction, the equilibrium constant is a definite constant value for each given temperature.

The equation of the equilibrium constant can show us what will happen if we change the concentration of any of the reactants involved in a reversible reaction. Such changes shift the chemical equilibrium. The change in the concentration caused by the upsetting of the equilibrium is known as the *equilibrium shift*.

The equilibrium shift produced by the change in concentration is a special case of a more general law known as Le Chatelier's Principle (1887) which can be formulated thus: *if any condition is changed in a system at equilibrium (temperature, concentration, pressure), the equilibrium will shift toward the process which tends to counteract the effect of the change.*

A rise in temperature intensifies an endothermic reaction and, conversely, the lowering of the temperature enhances an exothermic process.

Increasing pressure shifts the equilibrium towards the formation of fewer molecules, while if the pressure is lowered the reaction is intensified, thus increasing the number of molecules.

The increased concentration of substances found in one part of the equation stimulates the formation of products found in the other part of the equation.

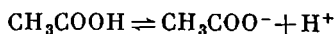
Hence, by changing the concentration of the reactants in equilibrated systems we can do the following:

- (1) remove a substance from a solution by adding an excess quantity of the other substance, provided their reaction is reverse;
- (2) convert a reversible process into a practically irreversible one by removing the products of the reaction.

## 3.2. Dissociation Constant

The law of mass action can be used to describe the state of various equilibrium systems.

Electrolytic dissociation\* is a reversible process which results in the establishment of an equilibrium. Electrolytic dissociation must therefore obey the law of mass action. For example, acetic acid dissociates into ions according to this equation



The equilibrium constant

$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

in the given case describes the electrolytic dissociation of acetic acid and is called the *dissociation constant*. The higher the dissociation constant, the stronger the ionization of the compound in question. The dissociation constant remains practically unchanged with the concentration of the solution, and it therefore gives a more general characterization of an electrolyte than the degree of dissociation.

There is a special relationship between the degree of dissociation  $\alpha$  (the value showing what part of the dissolved moles of the electrolyte has fallen into ions) and the dissociation constant. This relationship is described by the dilution law formulated by Ostwald:

$$\frac{\alpha^2}{1-\alpha} c = K$$

where  $\alpha$  is the degree of dissociation;  $c$  is the molar concentration of the electrolyte dissociating into two ions; and  $K$  is the dissociation constant.

Once two quantities in this equation are known, the third can be determined for the given conditions.

Such calculations give constant values for the quantity  $K$  only for weak electrolytes; for strong electrolytes  $K$  is not constant and increases with the concentration of the solution. This is obvious from Table 3.1 (see the value of  $K$  for the strong electrolyte, potassium chloride). For the purpose of comparison, the table also gives data for a weak electrolyte, acetic acid.

It follows therefore that the law of mass action is only applicable to weak electrolytes.

Solutions of strong electrolytes contain more ions than weak electrolyte solutions. The electrostatic interaction of ions is therefore more evident in strong electrolytes, and for this reason they do

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\* Electrolytic dissociation is a breakdown of molecules of electrolytes into ions by the action of a solvent.

Table 3.1

Dissociation Degree and Dissociation Constant of Electrolytes at 18°C

Electrolyte	Concentration	$\alpha$ , %	$K$
CH <sub>3</sub> COOH	0.1N	1.32	$1.76 \times 10^{-5}$
CH <sub>3</sub> COOH	0.01N	4.10	$1.75 \times 10^{-5}$
KCl	0.1N	86.20	0.536
KCl	0.01N	94.20	0.152

not obey the law of mass action and the value of  $K$  changes with dilution.

Table 3.2 gives dissociation constants of some electrolytes at 25°C.

Table 3.2

Dissociation Constants of Electrolytes

Electrolyte	$K$	Electrolyte	$K$
H <sub>3</sub> PO <sub>4</sub>		H <sub>2</sub> O <sub>2</sub>	$2 \times 10^{-12}$
$K_1$	$7.52 \times 10^{-3}$	CH <sub>3</sub> COOH	$1.76 \times 10^{-5}$
$K_2$	$6.23 \times 10^{-8}$	HCN	$4.79 \times 10^{-10}$
$K_3$	$2.20 \times 10^{-13}$	H <sub>2</sub> O	$1.86 \times 10^{-16}$
H <sub>2</sub> CO <sub>3</sub>		NH <sub>4</sub> OH	$1.79 \times 10^{-5}$
$K_1$	$4.31 \times 10^{-7}$		
$K_2$	$5.61 \times 10^{-11}$		

Since the dissociation constant of weak electrolytes is a constant value, the concentration of various ions in solution can be changed.

### 3.3. The Theory of Strong Electrolytes

According to the Debye-Hückel theory, strong electrolytes fully dissociate into ions. But the motion of particles in a liquid is obstructed by electrostatic forces acting between ions. Like in a crystal, each ion in a solution is surrounded by ions of the opposite sign, i.e. by the *ionic atmosphere*, which moves together with the central ion and limits its mobility. As a result, the electric conductivity of strong electrolyte solutions is less than one would expect if all the ions could freely move in an electric field. Hence, an impression is produced that the number of free ions in strong electro-

lyte solutions is less than their total (analytical) concentration. To characterize a strong electrolyte, the notion of an *effective* (i.e. actually seen in operation) *concentration of ions* is therefore introduced. This is known also as *activity*  $a$ . This value is similar to the concentration of free hydrated ions (according to the theory of electrolytic dissociation).

The relationship between the analytical concentration of a given ion  $c$  and its activity  $a$  is described by the equation  $a = fc$ , where  $f$  is the activity coefficient, the quantity analogous to the degree of dissociation  $\alpha$ .

The activity coefficient (like the degree of dissociation) tends to unity with dilution. For the case of infinite dilution, when the ions almost stop interacting, the activity of ions  $a$  becomes equal to their overall content  $c$  in the solution.

The activity coefficient depends on the ionic strength  $I$  of a solution and is connected with it by the following equation

$$\log f = \frac{-A\sqrt{I}}{1-\sqrt{I}}$$

where  $A$  is

$$\frac{1.823 \times 10^6 n_1 n_2}{(\epsilon T)^{3/2}}$$

$n_1$  and  $n_2$  are the charges on the ions,  $\epsilon$  is the dielectric constant of the solvent and  $T$  is the Kelvin temperature.

The *ionic strength of a solution*  $I$  is defined as half the sum of the products of the concentrations of all the ions in the solution by the square of their charge ( $n_i^2$ ). For example, if a solution contains 0.01 mole of  $\text{CaCl}_2$  and 0.1 mole of  $\text{Na}_2\text{SO}_4$  in 1000 g of water, then

$$I = \frac{1}{2} (0.01 \times 2^2 + 0.01 \times 2 \times 1^2 + 0.1 \times 2 \times 1^2 + 0.1 \times 2^2) = 0.33$$

The ionic strength of a binary electrolyte consisting of singly charged ions ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{AgNO}_3$ , and others) is  $C$ . Then, at  $t = 25^\circ\text{C}$ ,  $\log f = -0.509\sqrt{C}$ .

The higher the ionic strength of a solution, the higher is the solubility of sparingly soluble compounds in it.

**Example.** The solubility product of  $\text{CaSO}_4$  at  $25^\circ\text{C}$  is  $6.25 \times 10^{-5}$ . Determine the concentration of this salt, ignoring the ionic strength of the solution but taking account of the activity coefficients.

**Solution.** 1. Find the concentration of  $\text{CaSO}_4$  from the solubility product without taking account of the activity coefficients:

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}, \quad [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = x;$$

$$x^2 = K_{\text{sp}}; \quad x = \sqrt{6.25 \times 10^{-5}} = 7.91 \times 10^{-3}$$

The concentration  $[\text{CaSO}_4]$  is  $7.91 \times 10^{-3} \times 136 = 1.0757$  g/litre.

2. Determine the ionic strength of the solution,  $I$ :

$$I = \frac{1}{2} (7.91 \times 10^{-3} \times 2^2 + 7.91 \times 10^{-3} \times 2^2) = 31.64 \times 10^{-3}$$

3. Find the activity coefficient from ionic strength of the solution:

$$\begin{aligned} \log f &= -0.509 \cdot z^2 \sqrt{31.64 \times 10^{-3}} = \\ &= -0.509 \times 4 \times 1.78 \times 10^{-1} = -0.3624; \quad \log f = -0.3624, \quad \text{and} \quad f = 0.434 \end{aligned}$$

4. Determine the concentration of  $\text{CaSO}_4$  with taking account of the activity coefficients for the same system:

$$x = \sqrt{\frac{K_{sp}}{f_{\text{Ca}^{2+}} f_{\text{SO}_4^{2-}}}} = \sqrt{\frac{6.26 \times 10^{-5}}{0.434^2}} = \frac{7.91 \times 10^{-3}}{0.434} = 18.22 \times 10^{-3}$$

The concentration  $[\text{CaSO}_4]$  is  $18.22 \times 10^{-3} \times 136 = 2.4779$  g/litre.

The presence of extraneous salts also increases the ionic strength of solutions and increases the solubility of sparingly soluble substances. The phenomenon is known as the *salt effect*.

But the concentration of ions in saturated solutions of sparingly soluble electrolytes is so small and the forces interacting between the ions are so insignificant, that the coefficients of ion activity, for calculations of solubility of substances by the solubility product, are assumed to be unity ( $f = 1$ ). For example,  $K_{sp, \text{BaSO}_4} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x^2 = 1.1 \times 10^{-10}$ . Whence,  $x = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}$  mole/litre. If the solubility of salt is expressed in grams per litre, the number of moles is multiplied by the gram-molecular mass of  $\text{BaSO}_4$ :

$$x = 1.05 \times 10^{-5} \times 233.4 = 2.45 \times 10^{-3} \text{ g/litre}$$

## 3.4. Solubility Product

Sparingly soluble substances always have a saturated solution present over the precipitate. Ion exchange takes place between the solid solute and its solution. The ions of a solid substance pass from its surface into the solution, while a number of ions return from the solution to the solid substance.

Dynamic equilibrium is established between the dissolved and undissolved substance during the formation of a saturated solution. Consider a saturated solution of a sparingly soluble salt of silver chloride:  $\text{AgCl}_{\text{prec}} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ . Apply the law of mass action to this reversible system:

$$\frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]_{\text{prec}}} = K$$

where  $[\text{AgCl}]_{\text{prec}}$  is the concentration of silver chloride.

In a reversible system, precipitate  $\rightleftharpoons$  saturated solution, the equilibrium concentration of  $[\text{AgCl}]_{\text{prec}}$  at a given temperature is a constant value; it can be joined with the equilibrium constant.

The equation will then be

$$[\text{Ag}^+][\text{Cl}^-] = K[\text{AgCl}]_{\text{prec}} = K_{\text{sp, AgCl}}$$

The product of concentrations of electrolyte ions in a saturated solution characterizes the ability of the electrolyte to dissolve, and this value is therefore called the *solubility product* ( $K_{\text{sp}}$ ).

The sense of the equation is thus: *however the concentration of separate ions in a saturated solution of an electrolyte may change, the product of their concentrations at constant temperature remains unchanged.*

Once the solubility product of a given soluble salt is known, the amount of excess reagent required to lower the concentration of a particular ion to a wanted level, can easily be calculated.

**Example 1.** The solubility product of AgCl at 20°C is  $1.61 \times 10^{-10}$ . Determine the concentration of silver and chloride ions in a saturated solution of AgCl free from other soluble substances.

*Solution.*

$$[\text{Ag}^+][\text{Cl}^-] = 1.61 \times 10^{-10}$$

$$x = [\text{Ag}^+] = [\text{Cl}^-]$$

$$x = \sqrt{1.61 \times 10^{-10}} = 1.27 \times 10^{-5} \text{ g-ion/litre}$$

**Example 2.** Using the conditions of the previous example, determine the concentration of silver ions in an aqueous solution of 1N NaCl, saturated with respect to AgCl, and compare the result with that in the previous example.

*Solution.* The concentration of chlorine can be assumed to be equal to that of NaCl, i.e. 1 g-ion/litre, because the solubility of AgCl is so low compared with that of NaCl that the number of chloride ions liberated during the dissociation of AgCl can be disregarded.

$$[\text{Ag}^+] = \frac{K_{\text{sp, AgCl}}}{[\text{Cl}^-]} = \frac{1.61 \times 10^{-10}}{1} = 1.61 \times 10^{-10} \text{ g-ion/litre}$$

Hence, in the presence of NaCl the concentration of silver ions decreased  $\frac{1.27 \times 10^{-5}}{1.61 \times 10^{-10}} = 7.9 \times 10^4$ , i.e. 79,000 times.

Once the solubility product is known, the solubility of an electrolyte in water, the concentrations of cation and anion in a saturated aqueous solution, and also the quantity of precipitating agent required to separate the wanted ion, can be determined as well.

But it should be remembered that the solubility product rule holds only for sparingly soluble salts and only on the condition that the amounts of extraneous electrolytes contained in the solution are not high. Otherwise their ions will approach the surfaces of crystals and act on them with their electric field to appreciably change the conditions of dissolution.

Table 3.3 gives solubility products for some compounds.

Table 3.3

Solubility Products of Some Sparingly Soluble Substances

Substance	t, °C	$K_{sp}$	Substance	t, °C	$K_{sp}$
AgOH	20	$1.52 \times 10^{-8}$	AgCl	9.7	$0.37 \times 10^{-10}$
Al(OH) <sub>3</sub>			AgCl	25	$1.70 \times 10^{-10}$
after ageing (base)	25	$1.9 \times 10^{-33}$	AgCl	50	$13.2 \times 10^{-10}$
Ca(OH) <sub>2</sub>	18	$5.47 \times 10^{-6}$	AgCl	100	$21.5 \times 10^{-10}$
Fe(OH) <sub>3</sub>	18	$4.8 \times 10^{-16}$	Ag <sub>2</sub> CrO <sub>4</sub>	15	$1.2 \times 10^{-12}$
Fe(OH) <sub>3</sub>	18	$3.8 \times 10^{-38}$	AgI	25	$1.5 \times 10^{-16}$
Hg(OH) <sub>2</sub>	18	$1 \times 10^{-26}$	CaCO <sub>3</sub>	15	$9.9 \times 10^{-9}$
HgS	18	$4.0 \times 10^{-53}$	CaCO <sub>3</sub>	25	$4.8 \times 10^{-9}$
HgO	25	$1.7 \times 10^{-26}$	CaSO <sub>4</sub>	10	$6.1 \times 10^{-5}$
Hg <sub>2</sub> Cl <sub>2</sub>	25	$1.1 \times 10^{-18}$	CaSO <sub>4</sub>	25	$6.26 \times 10^{-5}$
Mg(OH) <sub>2</sub>	25	$5.5 \times 10^{-12}$	CaSO <sub>4</sub> ·2H <sub>2</sub> O	25	$1.3 \times 10^{-4}$
Mg(NH <sub>4</sub> ) <sub>4</sub> PO <sub>4</sub>	25	$2.5 \times 10^{-13}$	PbCO <sub>3</sub>	25	$1.5 \times 10^{-13}$
Zn(OH) <sub>2</sub>	25	$1.3 \times 10^{-17}$	BaSO <sub>4</sub>	25	$1.08 \times 10^{-10}$
FeS	25	$3.7 \times 10^{-19}$	BaSO <sub>4</sub>	50	$1.98 \times 10^{-10}$
FeCO <sub>3</sub>	20	$2.5 \times 10^{-11}$	Bi(OH) <sub>3</sub>	18	$4.3 \times 10^{-31}$
			CaF <sub>2</sub>	18	$3.4 \times 10^{-11}$
			CaF <sub>2</sub>	26	$3.95 \times 10^{-11}$

### 3.5. Distribution Law

Regenerative methods of water purification often involve extraction of the dissolved substances by other solvents in which a given substance is more soluble than in water. For example, if water is polluted with fats, oils, and resins, they can be extracted with carbon disulphide, CS<sub>2</sub>. Other liquids can also be used for the purpose but when selecting the liquid one should remember that it must not form a true solution with water.

Mixing together the two liquids gives a two-phase (two-layer) system in which the following processes occur:

(1) solute molecules pass from the aqueous layer into the carbon disulphide layer at the rate  $v_1$ ;

(2) as the solute is accumulated in the carbon disulphide, part of it returns into the aqueous layer at the rate  $v_2$ .

The rates at which the solute passes from one layer into the other are proportional to the concentration of the solute in each layer:  $v_1 = k_1 c_1$ ;  $v_2 = k_2 c_2$ , where  $k_1$  and  $k_2$  are proportionality coefficients;  $c_1$  is the concentration of the solute in the aqueous layer and  $c_2$  is the concentration of the solute in the carbon disulphide layer.

When the rates of the former and the latter processes become equal, a state of dynamic equilibrium is attained. Since  $v_1 = v_2$ ,

it follows that  $k_1c_1 = k_2c_2$ , or

$$\frac{c_1}{c_2} = \frac{k_2}{k_1} = K = \text{constant}$$

This mathematical expression of the distribution law can be understood as follows: *the ratio of concentrations of the solute distributed between two immiscible liquids is constant at a given temperature and does not depend on absolute or relative quantities of each solvent and the solute.*

The same law can also be formulated in this way: *the solute is distributed between two solvents proportionally to its solubility in each of the solvents; the ratio of the concentrations of the solute in the two solvents remains constant.*

The removal of the solute from water by another solvent is called *extraction*.

The distribution law is used to predict the efficiency of extraction of pollutants from water.

If the particle size of the solute remains unchanged during its distribution between two solvents, or the solute does not react chemically with either of them, the distribution law can be used to calculate the efficiency of the extraction process.

For example,  $A$  ml of water containing  $g_0$  g of extractable solute is treated with  $B$  ml of a solvent. The distribution coefficient is  $K = \frac{c_1}{c_2}$ , where  $c_1$  is the concentration of the solute in water, and  $c_2$  is its concentration in the solvent. Let the quantity of grams of the solute remaining in water after one extraction process be designated  $g_1$ , then

$$c_1 = \frac{g_1}{A}, \quad c_2 = \frac{g_0 - g_1}{B}$$

Substitute  $c_1$  and  $c_2$  into the formula of the distribution coefficient:

$$\frac{g_1 B}{A(g_0 - g_1)} = K$$

Transformations give the following

$$g_1 B = K A g_0 - K A g_1$$

now combine all members containing  $g_1$  in one part

$$g_1(B + KA) = K A g_0$$

Whence

$$g_1 = g_0 \frac{KA}{B + KA}$$

where  $g_1$  is the quantity of the solute remaining in the water after a single extraction process.

The amount of the substance that remains in the water after another extraction,  $g_2$ , is

$$g_2 = g_1 \frac{KA}{B + KA}$$

Substituting  $g_1$  into this equation we have the following expression

$$g_2 = g_0 \left( \frac{KA}{B + KA} \right)^2$$

After  $n$  number of repeated extractions with equal volumes of the solvent ( $B$  ml), the quantity of substance that remains in the water,  $g_n$ , can be found from the equation

$$g_n = g_0 \left( \frac{KA}{B + KA} \right)^n$$

whence the quantity of the extracted substance

$$g_{\text{ext}} = g_0 - g_n$$

Substituting the quantity  $g_n$  into this equation we have the following

$$g_{\text{ext}} = g_0 \left[ 1 - \left( \frac{KA}{B + KA} \right)^n \right]$$

**Example 1.** The distribution coefficient of iodine between amyl alcohol, ( $\text{C}_5\text{H}_{11}\text{OH}$ ), and water is  $K = 230$ . Calculate the concentration of iodine in the aqueous layer, if its equilibrium concentration in the alcohol layer is 2 g/litre.

*Solution.*

$$\frac{c_{\text{alc}}}{c_{\text{w}}} = 230; \quad \frac{2}{c_{\text{w}}} = 230;$$

$$c_{\text{w}} = \frac{c_{\text{alc}}}{230} = \frac{2}{230} = 0.0087 \text{ g}$$

The distribution law can be applied to concentrations not higher than 1*N*. For higher concentrations, the calculations will be only approximate.

## CHAPTER FOUR

# ACIDITY AND ALKALINITY OF SOLUTIONS. HYDROGEN ION CONCENTRATION

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### 4.1. Electrolytic Dissociation of Water

Water is a very weak amphoteric electrolyte dissociating into hydrogen cation and hydroxyl anion:  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ . The equilibrium is determined by the law of mass action

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = K_{\text{H}_2\text{O}}$$

This dissociation constant of water has been found experimentally, and at 25°C is  $1.86 \times 10^{-16}$ . Since the degree of dissociation of water is small, we shall not depart significantly from the truth if assume the concentration of undissociating molecules of water to be constant, and combine  $[\text{H}_2\text{O}]$  with the dissociation constant to express the equation as follows

$$[\text{H}^+][\text{OH}^-] = K_{\text{H}_2\text{O}}[\text{H}_2\text{O}] = K_w$$

where  $K_w$  is the *ionic product of water*.

The ionic product of water is a constant value at constant temperature. Its magnitude can be determined, since  $K$  and  $[\text{H}_2\text{O}]$  are known:  $K$  is  $1.86 \times 10^{-16}$  and the concentration of undissociated molecules of water is (due to the negligibly small dissociation) constant and equal to the total number of gram-molecules of water in a litre, i.e.  $1000 : 18 = 55.56$ . Hence,  $K_w = 1.86 \times 10^{-16} \times 55.56 = 1.0 \times 10^{-14}$  g-ion/litre.

The ionic product of water is an important value. It is constant for any concentration of hydrogen and hydroxyl ions in solution and only changes with temperature.

If the medium reacts neutral,  $[\text{H}^+] = 1 \times 10^{-7}$  g-ion/l. If a solution contains alkali or acid, the concentration of hydroxyl and hydrogen ions changes sharply, but the ionic product of water remains constant provided the temperature remains constant as well.

The ionic product of water helps us calculate the concentration of hydroxyl ion at a known concentration of the hydrogen ion, and vice versa. Any rise in the concentration of the hydrogen ion produces a corresponding reduction in the hydroxyl ion concentration.

For example, we want to determine the hydroxyl ion concentration in a solution, when the hydrogen ion concentration is  $1 \times 10^{-2}$  g-ion/litre.

$$[H^+][OH^-] = 1 \times 10^{-14};$$

$$[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12} \text{ g-ion/litre}$$

The ionic product of water can be used to give quantitative characteristics to any reaction of the medium (acid, neutral, or alkaline) via the hydrogen ion concentration.

The simple dependence of the hydrogen ion concentration on that of the hydroxyl ion (and vice versa) makes it possible to use either of them to characterize the alkalinity or acidity of a solution. The usual practice is to express alkalinity or acidity through the hydrogen ion concentration. In an acid medium this is higher than in an alkaline medium. It increases with acidity and decreases with the growing alkalinity of a solution.

For the sake of convenience, it is not the concentration of the hydrogen ion that is used to characterize the reaction of a solution but the logarithm of its reciprocal, known as the pH value

$$\text{pH} = -\log [H^+]$$

The pH value is expressed in gram-ions per litre. For example, if the hydrogen ion concentration  $[H^+] = 1 \times 10^{-5}$ , the pH is 5. And if  $[H^+] = 1 \times 10^{-7}$ , the pH is 7. The pH of a neutral medium is 7, that of an alkaline medium is greater than 7, and of an acid medium less than 7.

It should be noted that this holds only for the temperatures of 25°C. The dissociation of water absorbs much heat:



The degree of dissociation of water therefore greatly increases with heating, which thus increases the ionic product of water.

Table 4.1 illustrates the dependence on temperature of the ionic product of water  $K_w$  and the pH of a neutral medium.

It should also be emphasized that irrespective of temperature, the concentrations of hydrogen and hydroxyl ions are equal in a neutral medium.

Table 4.1

Dependence of Ionic Product of Water and pH on Temperature

Temperature, °C	Ionic product of water, g-ion/litre	pH of neutral medium
0	$1.139 \times 10^{-15}$	7.970
18	$5.702 \times 10^{-15}$	7.117
25	$1.008 \times 10^{-14}$	7.0 (6.999)
50	$5.474 \times 10^{-14}$	6.631
100	$5.9 \times 10^{-13}$	6.120

## 4.2. Active and Total Acidity

Two methods are used to describe quantitatively the acidity of a solution:

(1) to express the active acidity of a solution, the hydrogen ion concentration, or pH, value is used;

(2) total acidity is expressed by the normality of the solution, which is equal to the number of gram-equivalents of acid in one litre of solution.

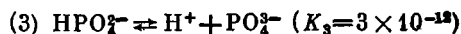
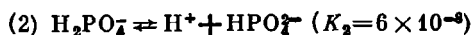
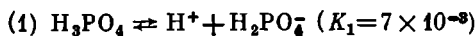
Consider the difference between active and total acidity.

In some reactions, for example, in reactions of indicators with solutions, only free ions of hydrogen, which are present in solution in given conditions, are involved. The hydrogen ion concentration (the pH value) characterizes this magnitude and expresses the *active acidity of solution*.

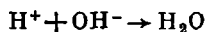
In other cases, all the hydrogen contained in an acid and capable of being separated in the form of the hydrogen ion  $H^+$ , can take part in the reaction.

In the titration of an acid solution with alkali, the hydroxyl ions bind free hydrogen ions in the first instance. As the concentration of these ions decreases, new acid molecules dissociate and all the hydrogen contained in the acid (not only the hydrogen which is present as free ions) can react.

An example of such a reaction is the neutralization of phosphoric acid with sodium hydroxide. Orthophosphoric acid is polybasic and a medium-strength electrolyte, whose dissociation degree  $\alpha$  is 27 per cent. It follows that only 27 out of 100 of its molecules dissociate into ions, the process occurring in steps:



Dissociation is easiest during the first stage. But if we increase the concentration of the hydroxyl ion  $OH^-$  in the acid solution, for example, by adding sodium hydroxide, the equilibrium can be shifted completely to the right, i.e. orthophosphoric acid can be completely dissociated. The equilibrium is shifted because the hydroxyl ions bind the hydrogen ions into a low-dissociating molecule of water:



*Total acidity is also known as analytical or titrated acidity.*

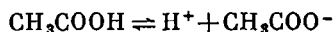
*Active acidity is only part of the total acidity and cannot be greater than it.*

The relationships between active and total acidity depend on the dissociation degree of acid in a given solution. The less the dissociation degree, the less is the fraction of active acidity in total acidity. Conversely, the difference between these two acidities is insignificant at high degrees of dissociation, and in the range where the dissociation degree is unity ( $\alpha = 1$ ) the active acidity is equal to total activity. This holds for dilute solutions of strong acids.

If we compare a strong and a weak acid, for example uninormal solutions of nitric and acetic acid, their total acidities are equal (normality is unity) but the active acidities will differ greatly. For nitric acid it is approximately  $[H^+] \approx 1$  g-ion/litre, and for acetic acid  $[H^+] = 0.0034$  g-ion/litre.

Consider the effect that the presence of a strong acid has on the dissociation degree of a weak acid, using hydrochloric and acetic acids as an example.

Assume that the solution contains acetic acid alone. Calculate the hydrogen ion concentration of this solution:



$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = K$$

Designate the concentration of the acid by  $c$ ;  $[H^+] = [CH_3COO^-] = x$ ;  $[CH_3COOH] = (c - x)$ ; we then obtain

$$K = \frac{x^2}{c - x}$$

Since  $x$  is very small compared with  $c$ , we can disregard it in the denominator. Then

$$K = \frac{x^2}{c}; \quad x = [H^+] = \sqrt{Kc}$$

*The hydrogen ion concentration in a weak acid solution is the square root of the product of its dissociation constant and the concentration.*

Let the concentration of acetic acid in a solution be  $0.1N$ . Its dissociation constant  $K = 1.76 \times 10^{-5}$ . Whence, the hydrogen ion concentration is

$$[H^+] = \sqrt{1.76 \times 10^{-5} \times 0.1} = 1.32 \times 10^{-3} \text{ g-ion/litre}$$

As we add hydrochloric acid with a concentration  $0.01N$  to the solution, the hydrogen ion concentration will be made up of two quantities: the concentration of hydrogen ions formed by the dissociation of  $HCl$  and the concentration of hydrogen ions formed by the dissociation of acetic acid. The former is  $10^{-2}$  and the latter  $x'$ .

It follows

$$[CH_3COO^-] = x' = [H^+]$$

whence

$$\frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = K = \frac{(10^{-3} + x')x'}{10^{-1}} = 1.76 \times 10^{-5}$$

By solving the equation we obtain  $x' = 1.7 \times 10^{-4}$ . Hence, the hydrogen ion concentration due to the dissociation of acetic acid has decreased eight times. It follows that by adding a great excess of a strong acid we can practically prevent the dissociation of a weak acid.

### 4.3. Acid-Base Indicators

Acid-base indicators are used to determine the reaction of the medium. They change their colour depending on the active acidity or alkalinity.

All acid-base indicators are very weak acids or weak bases.

If an indicator is an acid, it dissociates into ions as follows



and is characterized by the dissociation constant

$$K = \frac{[\text{H}^+][\text{Ind}^-]}{[\text{HInd}]}$$

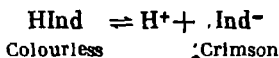
which is very small (for example, for phenolphthalein  $K = 1 \times 10^{-10}$ ).

The change in the concentration of hydrogen ion or hydroxyl ion strongly affects the dissociation degree of the indicator.

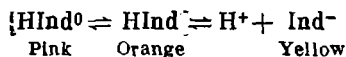
If an indicator is an acid, its dissociation is inhibited with the increasing concentration of the hydrogen ion, and conversely, its dissociation increases with the increasing concentration of the hydroxyl ion. If an indicator is a base, the dependence of its dissociation on the concentration of hydrogen and hydroxyl ions is reversed.

Indicators are classified as acid or alkaline depending on the medium in which their colour prevails.

Indicators are substances whose undissociated molecules differ in colour from their ions. Indicators which have a characteristic colour in only one medium and remain colourless in other media are known as *one-colour*. For example, phenolphthalein



Indicators which have different colours in an acid, alkaline, and neutral medium, are called *three-colour* indicators. For example, methyl orange:



HInd<sup>0</sup> is the isomeric form of the indicator, formed by the inner rearrangement of the atoms. Its colour may be different from that of undissociated molecules or of ions.

About 150 different indicators are known. Table 4.2 shows the pH ranges and characteristic colour of indicators in various media.

Table 4.2

Acid-Base Indicators

Indicator	pH														
	Acid medium							Alkaline medium							
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
para-Methyl red	R			Y											
Thymol blue	R			Y											
Tropeoline 00	R			Y											
Methyl orange			R		O-Y										
Bromcresol green			Y				B								
Methyl red					R		Y								
Litmus					R				B						
Bromphenol red					Y		R								
Bromthymol blue						Y		B							
Neutral red							R		Y						
$\alpha$ -Naphtholphthalein							Y-P			B-G					
Thymol blue	R			Y					Y		B				
Phenolphthalein									C			R			
Thymolphthalein										C			B		
Alizarine yellow										Y				Y	
Tropeoline 0											Y				O-Y
Orange G												Y			O-R

Symbols: C—colourless, Y—yellow, G—green, R—red, O—orange, P—pink, B—blue, and V—violet.

**Selecting an Indicator.** The process of neutralization of an acid with an alkali ends at the point of equivalence at pH 7. The reaction is often complicated by hydrolysis, the end of the titration process then often being attained at pH other than 7, the variations depending on the nature and concentration of the acids and alkalis involved. Therefore, a suitable indicator should be selected for each particular titration. The accuracy of a quantitative determination depends on the correct selection of an indicator.

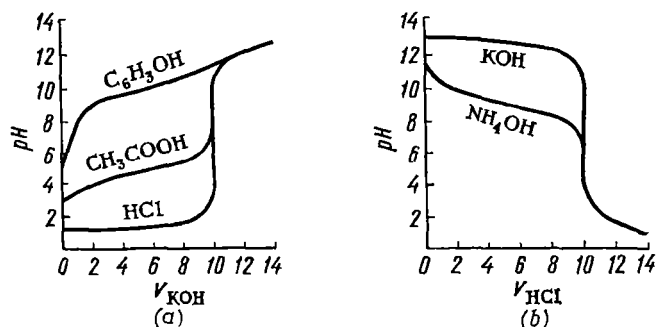


Fig. 4.1. Titration curves: *a*—acids; *b*—alkalis

The titration process is characterized by the pH values to which the solution is titrated with a given indicator. The range of pH values within which the colour of a given indicator changes is known as its *colour range*.

If a strong acid is titrated with a strong alkali, it makes virtually no difference which indicator is used, provided its colour range is within the limits of pH from 4 to 10, and the concentration of the solutions is about 0.1*N*. If dilute solutions are used, the pH range of indicators may be from 5 to 9. Methyl orange should not be used in such cases because its colour range extends beyond pH 4. It follows therefore that when selecting an indicator for each particular titration, only those indicators should be used whose colour range does not extend beyond the extremes of pH on the titration curve (Fig. 4.1).

As we have already said, indicators are weak electrolytes. Let us write down, in the general form, the dissociation constant and determine the hydrogen ion concentration:

$$\frac{[\text{H}^+][\text{Ind}^-]}{[\text{HInd}]} = K_d$$

Whence

$$[\text{H}^+] = K_d \frac{[\text{HInd}]}{[\text{Ind}^-]}$$

By taking logarithms and reversing the signs throughout, we obtain:

$$-\log [\text{H}^+] = -\log K_d - \log \frac{[\text{HInd}]}{[\text{Ind}^-]}$$

Substitute pH for  $-\log [\text{H}^+]$  and p*K* for  $-\log K_d$ . Then

$$\text{pH} = \text{p}K - \log \frac{[\text{HInd}]}{[\text{Ind}^-]}$$

The equivalence point is attained when the concentrations of  $[\text{HInd}]$  and  $[\text{Ind}^-]$  in solution become equal, i.e. when  $\text{pH} = \text{p}K$ , and the

colour range extends to one unit of pH on each side of the indicator exponent ( $pK$ ) ( $pH = pK \pm 1$ ).

The variations in pH ranges within which indicators change their colour are explained by their different dissociation constants. For example, at  $pK = 10$  the colour of phenolphthalein will change at pH from 9 to 11. The dissociation constant of lacmoid,  $K_d = 2.5 \times 10^{-6}$ ; therefore  $pH = pK = -\log 2.5 \times 10^{-6} = -(-6.0 + 0.4) = 5.6$ , and the colour range from pH 4.6 to 6.6.

If a weak acid is titrated with a strong alkali, the hydrogen ion concentration cannot be identified with the concentration of the acid. If the equivalence point has not been reached, the solution contains a mixture of a weak acid and its salt. For this mixture

$$[H^+] = K_d \frac{[HA]}{[A]}$$

or

$$-\log [H^+] = -\log K_d - \log \frac{c_{acid}}{c_{salt}}; \quad pH = pK - \log \frac{c_{acid}}{c_{salt}}$$

where  $c_{acid}$  is the concentration of the acid, and  $c_{salt}$  is the concentration of the salt.

Consider the neutralization of acetic acid with sodium hydroxide.  $K_d = 1.86 \times 10^{-5}$ , the  $pK = -\log 1.86 \times 10^{-5} = -(0.27 - 5) = 4.73$ . Hence the jump on the titration curve of acetic acid begins at  $pH = 4.73 - \log 0.001 = (4.73 + 3) = 7.73$  (i.e. at the ratio  $c_{acid}:c_{salt} = 0.1 : 99.9\% = 0.001$ ).

The end of the jump coincides with the moment when 0.1 per cent excess alkali is added. The excess builds up the concentration of  $[OH^-]$  in 1000 ml of solution:  $[OH^-] = \frac{0.1 \times 0.1}{100} = 0.0001 = 1 \times 10^{-4} M$ . Hence, at the end of the jump we have

$$[H^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10}; \quad pH 10.$$

The equivalence point will be  $pH = \frac{7.73 + 10}{2} = 8.87$ .

A weak base is titrated with a strong acid. Up until the moment when the equivalence point is attained,  $pH = 14 - pK_{base} + \log \frac{c_{base}}{c_{salt}}$ . At the equivalence point, the solution contains a salt of a weak base and a strong acid. For example, for the mixture  $NH_4OH$  and  $HCl$  ( $NH_4Cl$ )

$$pH = 7 - \frac{1}{2} pK_{base} - \frac{1}{2} \log c_{salt}$$

The equivalence point is at pH 5.12 and the jump extends from 4.12 to 6.12. Methyl orange can therefore be used as an indicator in this reaction.

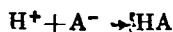
## 4.4. Buffer Solutions

If a strong acid or a strong base is added to water, the pH of the solution will change sharply even if the concentration of the acid or base is low. For example, if 0.01 g-equiv of HCl is added to 1000 ml of water, the hydrogen ion concentration (active acidity) in the solution will be  $1 \times 10^{-2}$  g-ion/litre, and the pH will be 2. Hence, the pH of the solution decreases from 7 to 2.

The addition of a strong alkali to water will likewise produce a sharp change in the hydrogen ion concentration of the solution. For example, we add 0.01 g-equiv of NaOH to 1000 ml of water. The pH increases from 7 to 12.

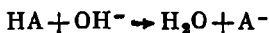
The picture is the same when strong acids or bases are added to solutions of salts formed by strong acids and strong bases.

The pH will change in quite a different way if we add a small amount of acid or alkali to a mixture of a weak acid and its salt. In this system, the hydrogen ion of the strong acid is bound in a molecule of a low-dissociating acid



The amount of the anion of a weak acid subjected to a reaction is replenished from the salt molecule.

As we add a strong alkali, the hydroxyl ions are bound to ions of hydrogen or of a weak acid:



The system is replenished with hydrogen ions from the remaining undissociated molecules of the weak acid.

The pH of the solution will not therefore vary greatly.

Consider a solution containing a mixture of  $CH_3COOH$  and  $CH_3COONa$  in concentrations of 0.1M. As 0.01 mole of HCl is added, the pH of the solution decreases from 4.73 to 4.64 (by 0.09).

This shows that the presence in the solution of a mixture of a weak acid and its salt controls the concentration of hydrogen ion and hydroxyl ion to lessen the effect of factors changing the pH of the solution. Such mixtures are known as *buffer solutions*.

**The Properties of Buffer Solutions.** 1. The hydrogen ion concentration in buffersolutions does not depend on dilution. This property of buffer solutions is employed in cases where constant pH is required.

2. The hydrogen ion concentration in a buffer solution changes only insignificantly on the addition of acids or bases.

But as we add an acid or a base, we must remember that the amount added should not exceed half the concentration of the salt or

the acid in the buffer. Otherwise the buffer capacity\* of the solution will be exceeded and the pH may change.

Buffer solutions are usually prepared from the following:

- (a) weak acids and their salts (e.g.  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ );
- (b) weak bases and their salts (e.g.  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ );
- (c) acid salts of polybasic acids (e.g.  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ ).

Each ratio of the concentrations of the two components forming a given buffer corresponds to a definite value of pH of the mixture. Commonly used buffer mixtures have been thoroughly studied and their pH values tabulated.

The pH value of a given buffer mixture can be calculated theoretically. Consider a buffer mixture consisting of a weak acid and its salt. Determine the hydrogen ion concentration from the equation of the dissociation constant for a weak acid:

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

The degree of dissociation of a weak acid can be disregarded, the concentration  $[\text{HA}]$  can be assumed to be equal to the concentration of the acid  $a$  g-equiv/litre, and the concentration of the ion  $[\text{A}^-]$  equal to the concentration of salt  $c$ , g-equiv/litre (for monobasic salts);

$$[\text{H}^+] = K \frac{a}{c}$$

Upon taking logarithms and changing the signs, this becomes:

$$\text{pH} = \text{p}K - \log \frac{a}{c}$$

Calculate the pH of a buffer mixture formed by weak bases and their salts from the formula

$$\text{pH} = 14 - \text{p}K + \log \frac{c_{\text{base}}}{c_{\text{salt}}}$$

The above equations are applicable to any buffer mixture. The equations show that the hydrogen ion concentration in a buffer solution depends on the dissociation constant of a weak acid (or a weak base) and on the ratio of the concentrations of the acid (or base) and the salt. The ratio  $\frac{c_{\text{salt}}}{c_{\text{acid}}}$  corresponds to the ratio of the solution's normality product and its volume. By varying the proportions of the acid and its salt, one can prepare a series of buffer solutions in which the pH changes gradually.

The phosphate buffer is very popular with chemists. It consists of a mono- and disubstituted salt of phosphoric acid, e.g.  $\text{NaH}_2\text{PO}_4$

\* The buffer capacity of a solution is determined by the number of g-equiv of a strong acid or alkali which needs to be added to 1000 ml of a buffer solution to change its pH one unit. The maximum buffer capacity corresponds to equivalent amounts of both components, the acid and the salt, in the solution.

and  $\text{Na}_2\text{HPO}_4$ . The acid component in this mixture is the ion  $\text{H}_2\text{PO}_4^-$  and the basic component, the ion  $\text{HPO}_4^{2-}$ . These ions are formed during dissociation of the salts and since they almost completely fall into ions in aqueous solutions, the ratio of the concentrations of the salts is equal to the ratio of the concentrations of their ions, i.e.

$$c_{\text{Na}_2\text{HPO}_4}/c_{\text{NaH}_2\text{PO}_4} = c_{\text{HPO}_4^{2-}}/c_{\text{H}_2\text{PO}_4^-}$$

Proteins, being amphoteric electrolytes, display the properties of both weak acids and weak bases and are therefore also used as buffers.

Buffer mixtures are very important in processes occurring in both living organisms and the mineral world. An example of a natural buffer is the blood of mammals. It always contains free carbonic acid and sodium carbonate. The pH of the blood is therefore always 7.4-7.7. The buffering action of soils is very important in agriculture, because plants absorb artificial fertilizers from the soil to change the hydrogen ion concentration in solutions that they extract from the soil in an unfavourable direction. An imbalance in the buffering action of soil is detrimental to useful microorganisms living in it.

Buffer solutions are very important in the treatment of domestic sewage, because the microorganisms which mineralize their organic matter develop better in a neutral medium. A deviation to acidity or alkalinity inhibits the vital processes in the microflora, thus adversely affecting the work of the purification plants.

Buffers play an important role in the chemical treatment of water to separate it from suspended matter of coagulation. The higher the buffer capacity of the treated water, the more efficient its purification with a hydrolyzing coagulant. The buffer capacity of natural water accounts for its neutralizing power.

Buffers are widely used in volumetric analysis; for example, an ammonium buffer ( $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ ) is used to determine calcium and magnesium ions in water (trilonometric method). Buffer mixtures are used to determine the pH of solutions colorimetrically (visually, by colour change) and potentiometrically (instrumentally, by measuring the e.m.f.).

## 4.5. Determining pH of Solution

**Colorimetric Methods.** These are based on the colour change of indicators in solution depending on the hydrogen ion concentration. The colour range of one indicator is very narrow, and a mixture of indicators is therefore used for approximate determinations of pH. The colour range of a mixture of indicators is very wide and covers pH values from strongly acid to strongly alkaline. The mixture is

known as a *universal indicator* and is used to locate the pH of a given solution within a certain range of pH values. More accurate determinations are arrived at by comparing the colour, intensity of a two-colour indicator in a given solution and in a standard buffer solution with a known pH. The procedure entails preparing a pH scale from a buffer mixture and in selecting an indicator whose colour range covers the approximate pH value of the solution in question. Then 5 ml of a 0.01*N* hydrochloric acid is placed in one test tube, another is filled with 5 ml of a 0.01*N* alkali, and the third one with 5 ml of the solution. Next, three drops of the chosen indicator solution are added to each test tube. If the colour of the solution is somewhere between the other two, the indicator has been selected correctly. Otherwise a new indicator should be tried.

**Determination of pH by the Michaelis Method (Without Buffer).** One-colour indicators are usually used in this method. These are nitro- and dinitrophenols whose acid form is colourless, while the alkaline is coloured. Unlike in the previous method, a scale is prepared from alkali solutions in which all the indicator added to the test tube is dissociated completely and the colour intensity can be considered to be proportional to the amount of the indicator added.

In order to determine pH by this method, a colour scale is prepared in which the colour intensity is proportional to the hydrogen ion concentration in solution (hence the pH).

**Potentiometric Determination.** This method is based on measuring the e.m.f. of a cell in which one of the electrodes is reversible with respect to hydrogen and the other is a reference electrode. The indicator (or measuring) electrode is selected according to the pH of the medium and the nature of the solution to be tested. For example, if the pH of a solution is within the range from 1 to 14, the hydrogen electrode can be used, provided this solution does not contain salts of metals which are less active (more noble) than hydrogen; nor should it contain cyanides or surfactants.

Solutions free from oxidants or reductants can be tested with a quinhydrone electrode (pH from 1 to 8). The same electrode can be used to determine pH in solutions of salts of metals less active than hydrogen, in alkaloid solutions, unsaturated organic acids, dilute nitric acid and its salts.

But the most reliable and accurate indicator electrode is glass. It is used for measuring pH from 2 to 11. Its potential does not depend on the presence in the solution of oxidants or reductants.

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## 4.6. Analysis Without Indicators

It is very convenient to examine the composition of coloured industrial effluents by electrometric methods, that is potentiometric and conductometric titrations.

**Potentiometric titration** is based on the linear dependence between the electrode potential and the hydrogen ion concentration in a solution. If the electrode used in titration is reversible with respect to the ions of the titrant or the titrand, the changing potential of this electrode during titration will indicate the change in the ion concentration in the solution.

Potentiometric titration can be used to determine the following: (a) neutralization reactions; (b) oxidation-reduction reactions; (c) reactions of precipitation and complexation.

All chemical reactions used in potentiometric titration should meet the following requirements:

(1) the reactions should proceed stoichiometrically, at a fast rate, and only in one direction; (2) the precipitating agents selected for the precipitation reactions should produce precipitates with the smallest possible solubility products; (3) those processes should be selected for the oxidation-reduction reactions in which the difference between the normal potential is the greatest; (4) the indicator electrode should be selected according to the type of the reaction underlying the titration.

Like usual titration, potentiometric titration is based on a sharp change in the concentration of the titrate in the vicinity of the equivalence point caused by the addition of a small quantity of a standard solution.

Accurate results can be obtained in the following cases: (1) titration of strong acids with strong bases and vice versa; (2) titration of weak acids with strong bases and vice versa (if the dissociation constant is not below  $1 \times 10^{-8}$ ); (3) titration of a mixture of acids of approximately equal concentrations but whose dissociation constants differ by not less than 100 times; (4) titration of multibasic acids if the ratio of the dissociation constants  $K_I : K_{II} = 10^4$ .

The determination of the concentration of substances by potentiometric titration entails measuring the potential of the indicator electrode on a potentiometer during neutralization of the solution and then constructing a titration curve.

The titration curve of a mixture of two acids has two slopes, the first of which corresponds to the neutralization point of a strong acid and the second, of a weak acid (see Fig. 4.2). If it is difficult to locate the neutralization points on the curve, a differential curve, as shown in Fig. 4.3, is used. The peaks of this curve correspond to the equivalence points.

**Conductometric Titration.** This method is based on measuring the conductivity of solutions. The character of changes in electrical conductivity during titration depends on the nature of the ions added, i.e. on their mobility and also on the formation of low-dissociating substances.

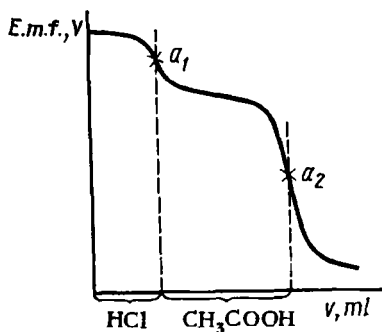


Fig. 4.2. Potentiometric titration curve for a mixture of a strong and a weak acid

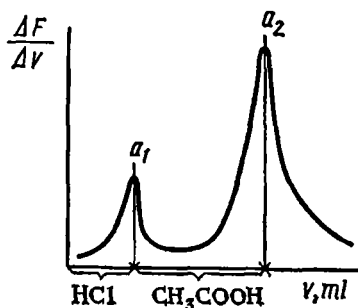


Fig. 4.3. Differential curve of potentiometric titration of a mixture of a strong and a weak acid

The dependence of the conductivity  $\chi$  on ion mobility is expressed by the equation  $\chi = \frac{c\alpha n}{1000} (\lambda_a + \lambda_c)$  where  $\lambda_a$  and  $\lambda_c$  are the mobilities of the ions;  $\alpha$  is the dissociation degree of the electrolyte;  $n$  is the valency of the ions; and  $c$  is the concentration, g-equiv/litre.

The equivalent conductivity of an electrolyte is related to mobility as follows:  $\lambda_\infty = \lambda_c + \lambda_a$  (Kohlrausch's equation). The equivalent conductivity at infinite dilution is equal to the sum of the limit mobilities of the ions. Hence, if one ion is substituted for another during titration as a result of chemical reaction, the resistance of the solution changes, this then changing the electrical conductivity.

Experimental curves showing the changes in the conductivity resulting from the number of millilitres of standard solution (titrant) added are known as *conductometric* curves. The equivalence point is located at the bend in the curve because excess reagent, added after the equivalence point has been attained, increases conductivity.

The conductometric curve of a strong acid titrated with a strong base is shown in Fig. 4.4. Analysis of the curves shows the nature of changes in the conductivity of separate components in the solution. The summary straight line  $ao$  represents the concentrations of the acid and the salt;  $ad$  is the acid straight line;  $co$  is the salt straight line;  $ob$  is the summary straight line representing the conductivity of the salt  $oe$  and the free base  $de$ . The acid and the alkali lines intersect at the equivalence point.

Conductometric titration can be used to determine the concentrations of mixtures of acids of various strengths. The corresponding titration curves have as many bends as the mixture contains acids (Fig. 4.5).

The first bend shows the equivalence point ( $b$ ) corresponding to the amount of the stronger acid, while the subsequent bends are arranged in the order of their decreasing strength.

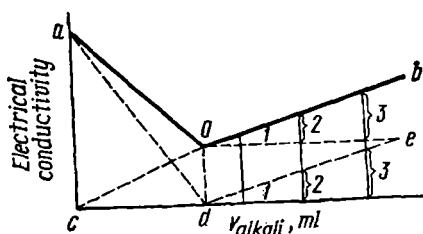


Fig. 4.4. Curves of conductometric titration by a neutralization reaction

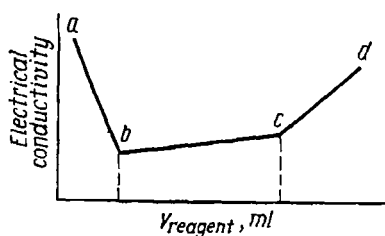


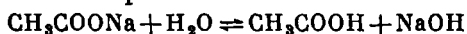
Fig. 4.5. Conductometric titration curves for a mixture of two acids: *ab*—strong acid; *bc*—weak acid

The observed increase in conductivity after neutralization of the strong acid along the line *bc* (Fig. 4.5) corresponds to the formation of a completely dissociating salt of a weak acid; the increasing conductivity along the line *cd* is due to the appearance of a free strong base. In conductometric titration the value of the electrical conductivity of a solution is determined by the total number of ions present in it, irrespective of whether or not they are involved in the reaction. To be sure that the results are correct, one must exclude extraneous electrolytes which do not participate in the reaction from the solution.

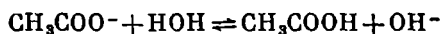
## 4.7. Hydrolysis of Salts

Hydrolysis is the exchange decomposition of substances by water. Hydrolysis is a special case of exchange interactions between solute and solvent, known as *solvolysis*.

During hydrolysis, cations or anions of salts bind hydrogen ions or hydroxyl ions of water to form low-dissociating or sparingly soluble products. Free ions of hydroxyl or hydrogen are accumulated in this process. For example, during dissolution in water of sodium acetate (the salt of a weak acid and a strong base) the following chemical reaction takes place:



or, in ionic form:



Acetic acid (a low-dissociating substance) binds the hydrogen ion. Hence, *hydrolysis is the chemical interaction of ions of a dissolved salt with water, which behaves like solvent, and is associated with the change in the reaction of the medium.*

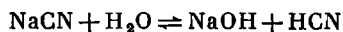
Salts of weak acids and weak bases, of weak acids and strong bases, and of strong acids and weak bases are subject to hydrolysis. Salts formed by a strong acid and a strong base are not hydrolyzed.

Hydrolysis is a slow process and equilibrium is attained over a period of time. This is why the pH of solutions of hydrolyzable salts changes only over time.

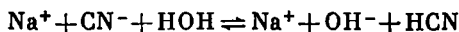
The extent of hydrolysis is characterized by its *degree  $\beta$* , which is the ratio of the number of hydrolyzed molecules of the salt to the total number of salt molecules in the solution. As a rule it is expressed in per cent.

A convenient method of expressing quantitatively the degree of hydrolysis is the hydrogen ion concentration (pH) of the solution.

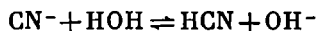
Consider the hydrolysis of sodium cyanide, NaCN, a salt formed by a weak acid and a strong base. (The degree of dissociation of a 0.1N solution of hydrocyanic acid is 0.01%, and the apparent degree of dissociation of a 0.1N solution of sodium hydroxide at 18°C is 84 per cent). When dissolved, this salt reacts with water according to the equation:



Write down the equation in the ionic form



Cancel the ions which do not take part in the reaction to obtain the ionic equation of the hydrolysis of sodium cyanide:



Now apply the law of mass action to this reversible process:

$$\frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-][\text{HOH}]} = K$$

The concentration of undissociated water molecules, compared with the concentration of hydrolyzed molecules, is an infinitely great quantity. We can assume it to be a constant and move it to the right part of the equation with replacement of the product of two constants by one constant, the *hydrolysis constant*:

$$\frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]} = K[\text{HOH}] = K_{\text{hydr}}$$

To determine the hydrolysis constant of NaCN, perform the following conversions. Determine the concentration of the hydroxyl ion from the ionic product of water and substitute it into the equation expressing the constant:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}; \quad \frac{[\text{HCN}]K_w}{[\text{CN}^-][\text{H}^+]} = K_{\text{hydr}}; \quad \frac{[\text{HCN}]}{[\text{CN}^-][\text{H}^+]} = \frac{1}{K_{\text{HCN}}}$$

where  $K_{\text{HCN}}$  is the dissociation constant of hydrocyanic acid. It follows:

$$\frac{K_w}{K_{\text{HCN}}} = K_{\text{hydr}}$$

or in the general form

$$\frac{K_w}{K_{HA}} = K_{hydr}$$

where  $K_{HA}$  is the dissociation constant of a weak acid.

*The hydrolysis constant of a salt of a strong base and a weak acid is equal to the ionic product of water divided by the constant of dissociation of the weak acid.* Or, in other words, the hydrolysis constant is determined by the dissociation constant of a weak acid or a weak base.

During hydrolysis of salts formed by a weak base and a strong acid, the hydrolysis constant is equal to the ionic product of water divided by the dissociation constant of the weak base:

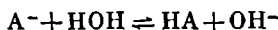
$$K_{hydr} = \frac{K_w}{K_{d. base}}$$

During hydrolysis of salts formed by a weak base and a weak acid, the hydrolysis constant is equal to the ionic product of water divided by the product of the dissociation constants of the base and the acid:

$$K_{hydr} = \frac{K_w}{K_{acid}K_{base}}$$

Once the hydrolysis constant is known it is easy to determine the hydrogen ion concentration in a solution of a hydrolyzed salt, because pH is a factor which characterizes the hydrolyzing properties of a salt.

If hydrolysis proceeds according to the equation



the hydrolysis constant will be

$$\frac{[HA][OH^-]}{[A^-]} = K_{hydr}$$

Since only a small part of molecules undergo hydrolysis, the concentration of the ion  $A^-$  can be equalized with the concentration of the dissolved salt  $c$ . The concentrations of the ion  $OH^-$  and molecules  $HA$  are equal, according to the ionic equation. Designate their concentrations by  $x$  and substitute them into the hydrolysis constant:  $x^2/c = K_{hydr}$  or

$$x = [OH^-] = \sqrt{K_{hydr} \times c}$$

**Example 1.** Calculate the pH of a 0.01N solution of sodium acetate;  $K_{CH_3COOH} = 1.76 \times 10^{-5}$ .

*Solution.* Determine the concentration of the hydroxyl ion in the solution:

$$[OH^-] = \sqrt{K_{hydr}c} = \sqrt{\frac{K_w}{K_{CH_3COOH}}} c = \sqrt{\frac{10^{-14}}{1.76 \times 10^{-5}}} 10^{-2} = 7.3 \times 10^{-6}$$

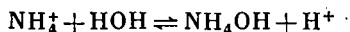
Determine the hydrogen ion concentration from the ionic product of water:

$$[\text{H}^+] = \frac{10^{-14}}{7.3 \times 10^{-6}} = 1.4 \times 10^{-9}$$

$$\text{pH} = -\log[\text{H}^+] = 9 - 0.146 = 8.854 = 8.85$$

**Example 2.** Calculate the pH of a 0.1*N* solution of ammonium chloride;  $K_{\text{NH}_4\text{OH}} = 1.75 \times 10^{-5}$ .

*Solution.* Write the ionic equation of the hydrolysis of ammonium chloride:



Determine the hydrogen ion concentration from the hydrolysis constant equation:

$$[\text{H}^+] = \sqrt{K_{\text{hydr}}c} = \sqrt{\frac{K_w}{K_{\text{NH}_4\text{OH}}}}c = \sqrt{\frac{10^{-14}}{1.75 \times 10^{-5}}}10^{-1} = 7.5 \times 10^{-6}$$

$$\text{pH} = 5.13$$

The degree of hydrolysis of a given salt depends, in the general case, on the temperature, concentration, and pH of the solution.

Rising temperature increases the dissociation of water to increase the concentration of hydrogen and hydroxyl ions. The same effect is produced by the decreasing concentration of the solution during hydrolysis of salts formed by a weak base and a strong acid or a strong base and a weak acid. Therefore, in order to intensify hydrolysis solutions should be more diluted and the temperature should be raised, and vice versa; to lessen hydrolysis the reverse is required.

If any product of hydrolysis is liberated from a solution, either in the form of a precipitate or vapour, this promotes hydrolysis as well, and in most cases results in full hydrolysis of the initial salt.

A salt formed by a strong acid and a weak base hydrolyses better at low concentration of the hydrogen ion, while a salt formed by a strong base and a weak acid is better hydrolyzed at high hydrogen ion concentration.

For example, the hydrolysis of  $\text{AlCl}_3$  in moderately dilute solutions at room temperatures ceases at the first stage:



and the second stage begins only at low concentrations of the solution:



Complete hydrolysis to the point of the formation of a free base  $\text{Al}(\text{OH})_3$  at room temperature, even with high dilution, is prevented by the accumulation in the solution of the hydrogen ion. And the equilibrium of the reaction can be shifted to the right only by binding the hydrogen ion with the hydroxyl ion.

The hydrolysis constant is connected with the degree of hydrolysis by the following equation

$$\frac{\beta^2}{1-\beta} c_{\text{salt}} = K_{\text{hydr}}$$

This equation is valid for salts formed by a strong acid and a weak base and by a weak acid and a strong base.

For low hydrolyzing salts, when  $\beta \ll 1$ , the denominator can be assumed to be unity; the degree of hydrolysis will then be

$$\beta = \sqrt{\frac{K_{\text{hydr}}}{c_{\text{salt}}}}$$

The hydrolysis constant for salts formed by a weak acid and a weak base has the following expression:

$$K_{\text{hydr}} = \frac{\beta^2}{(1-\beta)^2}$$

This equation shows that  $K_{\text{hydr}}$  of salts of a weak acid and a weak base does not depend on the concentration of the salt. For low-hydrolyzing salts, where  $\beta \ll 1$ , the degree of hydrolysis is

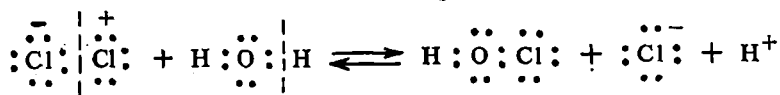
$$\beta = \sqrt{K_{\text{hydr}}}$$

## 4.8. Hydrolysis of Chlorine

As chlorine is dissolved in water, it is hydrolyzed\* according to this equation:



The hydrolysis is supposed to be preceded by polarization of the covalent bond between the chlorine atoms in the molecule, i.e. the displacement of the shared electron pair toward one of the atoms under the effect of polar molecules of water:



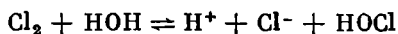
The equilibrium in this reaction is strongly shifted to the left. Hence, as chlorine reacts with water, insignificant quantities of hydrochloric and hypochlorous acids are formed. But the equilibrium of chlorine with water can be shifted quantitatively to the right by adding an alkali, e.g.



Hydrolysis of chlorine was first studied by A. A. Yakovkin (1863-1936), who determined the equilibrium constant of this reaction and the degree of hydrolysis of chlorine at various temperatures.

\* This reaction can be regarded as an oxidation-reduction process because one chlorine atom donates its electron and the other atom accepts it.

A solution of chlorine water contains only ions of hydrochloric acid because hypochlorous acid is very weak (its dissociation constant at 18°C is  $2.95 \times 10^{-8}$ ) and the presence of a strong acid in the solution inhibits the dissociation of hypochlorous acid. The ionic form of this equation is as follows:



The hydrolysis constant will be

$$\frac{[\text{H}^+][\text{Cl}^-][\text{HOCl}]}{[\text{Cl}_2]} = K[\text{H}_2\text{O}] = K_{\text{hydr}}$$

The experimental determination of this constant gives  $K_{\text{hydr}} = 4.5 \times 10^{-4}$ .

From this constant, it is possible to determine the concentration of free chlorine in water at any initial concentration.

Designate the initial concentration of chlorine by  $a$ , the concentration of chlorine at the moment of equilibrium by  $a - x$ , and the concentrations of HOCl,  $\text{H}^+$  and  $\text{Cl}^-$ , which according to the last equation are equal, by  $x$ . Put these letters into the hydrolysis constant to obtain the following equation.

$$\frac{x^3}{a-x} = 4.5 \times 10^{-4}$$

$$x^3 + 4.5 \times 10^{-4}x - 4.5 \times 10^{-4}a = 0$$

This cubic equation is easy to solve graphically with a cubic parabola and an intersecting inclined straight line.

The reduced equation  $x^3 - (4.5 \times 10^{-4}a - 4.5 \times 10^{-4}x) = 0$  can be rearranged as follows:  $y = x^3$  and  $y = 4.5 \times 10^{-4}a - 4.5 \times 10^{-4}x$ .

The parabola is constructed by the equation  $y = x^3$  and the straight line by the equation  $y = 4.5 \times 10^{-4}a - 4.5 \times 10^{-4}x$ .

A perpendicular, dropped from the point of intersection of the straight line and the parabola to the  $x$ -axis, cuts off a line segment on it (from the origin to the point of intersection) corresponding to the amount of hydrolyzed chlorine.

An example of the graphical determination of hydrolyzed chlorine in water is given in Fig. 4.6.

Determine the coordinates of the points of the parabola and construct it:

$$\begin{array}{ll} x_1 = 0.05; & y_1 = 0.05^3 = 0.000125 \\ x_2 = 0.1; & y_2 = 0.1^3 = 0.001 \\ x_3 = 0.15; & y_3 = 0.15^3 = 0.003375 \\ x_4 = 0.2; & y_4 = 0.2^3 = 0.008 \end{array}$$

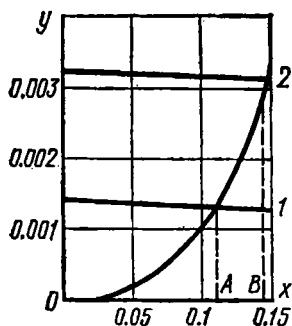


Fig. 4.6. Graphical determination of hydrolyzed chlorine in water

Next determine the coordinates of the straight line for  $a = 3$  mg/l:

$$y = -0.00045x + 0.00135$$

$$x_1 = 0; y_1 = 0.00135$$

$$x_2 = 0.15; y_2 = -0.0000675 + 0.00135 = 0.0012825$$

$$x_3 = 0.2; y_3 = -0.00009 + 0.00135 = 0.00126$$

As we drop a perpendicular from the point of intersection of the straight line and the parabola, it intersects the x-axis to mark off a line segment from the point A to point O ( $OA = x = 0.109$ ).

Hence the concentration of free chlorine at the moment of equilibrium is

$$3 - 0.109 = 2.891$$

If the initial concentration of chlorine  $a = 7$  mg/litre, then, by constructing the straight line for  $a = 7$ , we can also find the quantity of hydrolyzed chlorine:

$$y = -0.00045x + 0.00315$$

$$x_1 = 0; y_1 = 0.00315$$

$$x_2 = 0.15; y_2 = 0.0030825$$

Now draw a perpendicular from the point of intersection of the straight line and the parabola to the x-axis at the point B, and determine the concentration of hydrolyzed chlorine:

$$OB = x = 0.146$$

The concentration of chlorine at the point of equilibrium will then be

$$7 - 0.146 = 6.854 \text{ mg/litre}$$

## CHAPTER FIVE

# THE PHASE RULE

The law of mass action describes the behaviour accompanying equilibrium in homogeneous systems. The same behaviour for heterogeneous systems is expressed by the phase rule, formulated by J. Gibbs in 1876-1878.

In order to study the phase rule one must first acquaint oneself with the concepts of *system*, *phase*, *independent component*, and *degrees of freedom*. It also is necessary to establish the general regularities observed at equilibrium between phases.

*A system is a body or a group of bodies which interact and are assumed to be separated from the environment.*

A homogeneous system is an aggregation of molecules, either similar or different, but with uniformity of composition and inner structure.

A heterogeneous system contains molecular aggregations, different in either composition or inner structure and separated from one another by an interface.

*A phase is a homogeneous part of a heterogeneous system separated from other parts by an interface.* A phase can be mechanically isolated from the system.

Although a phase is homogeneous in the physical sense, it can consist of molecules of different types. For example, a solution of sugar in water is a one-phase system. Gas and vapour mix in any proportion; they are not separated from each other by any interface. Therefore, a system consisting of gas and vapour is always a *one-phase system*. Liquids that can be mixed in any proportion, such as water and alcohol, acetone and alcohol, also form one-phase systems. Unsaturated solutions of solid substances in liquids are also one-phase systems.

Partially miscible liquids, for example, water and ether, form a *two-phase system*. A system remains two-phase even in cases where one phase is reduced to fine grains or drops, for example, suspensions (sand in water), or emulsions (kerosine in water). A solid solution is a one-phase system, while an eutectic alloy is a two-phase system.

A system can consist of similar or different molecules. For example, steam and liquid water consist of the same molecules  $H_2O$ ,

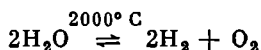
while a solution of sugar in water contains molecules of two types (sugar and water).

*Chemically specific substances that form a given system and can exist in an isolated form independently, are called constituents of a system.* According to this definition, ions cannot be considered constituents of a system because they cannot exist outside the system.

Systems are classified as *physical* and *chemical*. Chemical reactions do not occur in physical systems, while in chemical systems reversible chemical processes between constituents take place.

For example, at low temperatures (up to 200°C), a gaseous mixture of  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{H}_2$  is a physical system in the absence of a catalyst, and no chemical processes occur in it. The number of molecular species in the system is three.

At a temperature of 1000-2000°C this physical system turns into a chemical one, because all three constituents become involved in a reversible chemical process:



It is impossible to change arbitrarily the concentration of all three constituents in a chemical system at equilibrium, because if we change the concentration of two constituents, the concentration of the third will change automatically.

Substances whose concentrations in a chemical system at equilibrium can be arbitrarily determined beforehand are known as independent constituents or components of a system.

Substances whose concentrations in a system at equilibrium depend directly on the chemical processes which occur in the system are dependent constituents of the system. The choice of the number of components is often a difficult problem. The following rule is therefore recommended.

*The number of components in a system at equilibrium is equal to the number of constituents less the number of chemical equations according to which the substances forming the system react reversibly between themselves under the given conditions of the system.* For example, in a closed system  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ , at a temperature of about 900-1000°C (limestone roasting) the process is reversible. The three constituents of this system are interconnected by one reversible process. Hence, the number of components in it is two.

The above rule shows that *the number of components in a chemical system is always less than the total number of constituents in it.* In the absence of chemical processes, i.e. in a physical system, *the number of components is equal to the number of constituents.*

A system consisting of water, vapour and ice, is heterogeneous. It consists of three phases, solid, liquid, and gaseous. All three phases are at equilibrium under certain conditions. Hence, the phase diagram of water (Fig. 5.1) shows the dependence between the

water vapour pressure and the temperature, and also the conditions of the simultaneous existence of water in various phases. Each point on the curves corresponds to equilibrium between two phases. The curve  $AO$  shows the equilibrium in the ice-vapour system; the curve  $OD$ , the equilibrium in the supercooled water-vapour system;  $OC$ , the equilibrium in the water-vapour system; and  $OB$ , the equilibrium in the ice-liquid water system.

The curves  $AO$  and  $OC$  show the pressure of saturated vapour over liquid water (curve  $OC$ ) and over ice (curve  $AO$ ). Each temperature corresponds to a certain pressure, while conversely, each pressure corresponds to the specific temperature at which water and vapour are at equilibrium.

For example, at a temperature of  $100^{\circ}\text{C}$  both phases are at equilibrium only under a pressure of 760 mm Hg. If the pressure is raised, the vapour condenses, and if lowered, the water begins to evaporate.

At point  $O$  the curve of the vapour pressure over the liquid water is intersected by the curve of the vapour pressure over the ice. This point of intersection corresponds to the equilibrated state of all three phases:



The point corresponding to the equilibrium of all three phases is the *triple point*. This point is attainable only under a pressure of 4.6 mm Hg (more exactly, 4.579 mm Hg) and a temperature of  $0.01^{\circ}\text{C}$  ( $0.0098^{\circ}\text{C}$ ).

The state of a system is characterized by its factors (conditions).

*The number of factors (temperature, pressure, concentration) which can be changed within certain limits without altering the number or type of phases in the system is called the number of degrees of freedom.*

The number of degrees of freedom at a triple point is zero. The degree of freedom of an unsaturated solution is two, i.e. without changing the number of phases we can change two factors: the concentration and temperature. An ideal gas, characterized by the Clapeyron equation  $pv = RT$ , or  $p = cRT$ , because  $c = \frac{1}{v}$ , has two degrees of freedom, i.e. we can, without changing the number of phases in the system, change two factors:  $p$  and  $T$ ,  $c$  and  $T$ , or  $c$  and  $p$ .

The quantitative connection between the number of phases, the number of components, and the number of degrees of freedom is expressed by the *phase rule*, which reads as follows: *in a system at equi-*

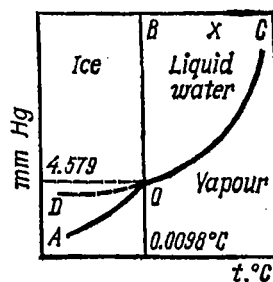


Fig. 5.1. Phase diagram for water

*librium, the sum of the number of phases  $P$  and the number of degrees of freedom  $F$  is equal to the sum of the number of components  $C$  and the number of external factors affecting the equilibrium of the system:*

$$P + F = C + n$$

The  $n$  is usually equal to 2 (i.e. two factors: temperature and pressure) but it can also be greater than 2 if other factors effect the system, or less than 2, as is the case with metal alloys where pressure cannot have any effect. For liquid systems,  $P + F = C + 2$ .

**Example 1.** Determine the number of phases in a saturated salt solution.  
*Solution.*

$$P = C + 2 - F = 2 + 2 - 1 = 3$$

In a saturated solution, the one degree of freedom is temperature, and the number of phases is three: solid, liquid, gaseous.

**Example 2.** Determine the number of degrees of freedom at the triple point of the phase diagram for water.

*Solution.*

$$F = C + 2 - P = 1 + 2 - 3 = 0$$

The number of degrees of freedom is zero.

**Example 3.** Determine the number of degrees of freedom at point  $x$  (Fig. 5.1) lying inside the liquid phase.

*Solution.*

$$F = C + 2 - P = 1 + 2 - 1 = 2$$

The system at point  $x$  has two degrees of freedom: temperature and pressure.

**Example 4.** Determine the number of phases in an unsaturated solution.  
*Solution.*

$$P = C + 2 - F = 2 + 2 - 2 = 2$$

The number of phases is two: liquid and gaseous.

## CHAPTER SIX

# THE COLLOIDAL STATE

A disperse system, with particles ranging in size from 1 to 100 milimicrons distributed in a suitable medium, is called a colloidal solution or sol.

When speaking of colloids, we mean a special state of matter characterized by a certain dispersity (reduction of size by milling or grinding). In the colloidal state, matter is reduced to very small particles or is full of the minutest pores. The size of these particles or pores exceeds that of a molecule, and when aggregated the particles form a phase separated from the medium by the interface. Hence, the colloidal system is a heterogeneous one consisting of two (or more) phases, namely the disperse phase (one or several), which is the aggregation of particles or pores, and the medium in which the former phase is dispersed.

The essential properties of colloidal systems are associated with the free interface energy. The amount of this energy depends on the specific surface of a particle  $s_0 = \frac{s}{v}$ , where  $s$  is the total surface area,  $v$  is the volume of the disperse phase. It has been established that the specific surface  $s_0$  increases with the degree of dispersion in inverse proportion to the linear dimensions of the particles; in the colloidal region the specific surface is immense. For example, with particles of the edge length  $1 \times 10^{-6}$  cm, the specific surface is as large as  $6 \times 10^6$  sq. cm, or 600 sq. m per cu. cm of the disperse phase. But the specific surface increases only to the limit of the colloidal state, because further reductions in particle size can destroy the interface between the disperse phase and the dispersion medium, and free interface energy disappears (Fig. 6.1). The system becomes homogeneous, i.e. a true solution is formed.

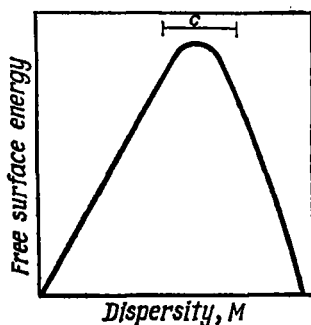


Fig. 6.1. Dependence of the free interphase energy of a substance on its dispersity: C—colloidal dispersity region; M—molecular dispersity region

To summarize, the basic and most important property of the colloidal state is that a considerable proportion of the entire mass and free energy of the system is concentrated at the interface.

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## 6.1. Classification of Colloidal Systems

There are different classifications of colloidal systems.

**Classification by the state of aggregation of the dispersion medium.**

According to this classification *aerosols* are the colloidal suspension of particles in a gas (smoke, fog, etc.); *lyosols* are systems in which particles are suspended in a liquid (if the liquid is water, the system is called hydrosol, e.g. clay, sand in water); *soliosols* are systems in which the disperse system is distributed in a solid (alloys, coloured glass, some minerals).

**Classification by the Interaction at the Interface.** The interface is always the site of the interaction between the disperse phase and the dispersion medium. This interaction is due to the interface free energy (noncompensated van der Waals' forces) but its effects vary for different substances. The disperse systems can be *lyophilic* (from Greek *lyein* to loose, dissolve, and *philos*, loving) or *lyophobic* (*phobos*, fear). Lyophilic systems are characterized by the strong affinity between the disperse phase and the dispersion medium, while lyophobic systems lack this strong affinity. Solvate envelopes (hydrate envelopes, if water is the dispersion medium) are formed around the dispersed particles through the intermolecular action.

Lyophilic colloidal systems are formed mostly by substances with high molecular mass. These substances are lyophilic to certain media and dissolve in them spontaneously or swell to form jellies.

High-molecular compounds differ from ordinary solid substances. They are not volatile and cannot be sublimed. They are readily destroyed by the action of external factors (oxygen or other destructive agents) which significantly alter their original properties. Depending on temperature, high-molecular compounds can be either highly viscous, hyperelastic, or solid (glassy or crystalline).

**Classification by the Inner Structure of Particles.** Disperse systems are divided into two main classes, depending on their inner structure.

**Suspensoids\* and molecular colloids.** *Suspensoids* are highly dispersed heterogeneous systems (lyophilic or lyophobic), unstable and irreversible, whose particles are aggregations of atoms or molecules separated from the medium by the interface. They include sols of

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\* A suspensoid (resembling suspension) differs from a true suspension by the particle size. A suspension is a coarsely dispersed system (solid in liquid).

metals, their oxides, hydroxides, various mineral salts, etc. The particles of these sols have the inner crystalline structure of the corresponding compact substance. They are called lyophobic because of their weak interaction with the dispersion medium. They are irreversible because their dry residue does not form sols on contact with the dispersion medium. The properties of suspensoids are determined by the high interface energy, which accounts for their instability in the absence of stabilizing agents. Ions, molecules, and high-molecular compounds can be used as stabilizers. The ionic stabilization can be explained by the adsorption of ions in the dispersion medium or by the dissociation of molecules on the surface of the particle nucleus.

High-molecular compounds are adsorbed on the surface of the particle to form, in the surface layer, reticular or gel-like structures which prevent the aggregation of particles. These are called protective colloids, and the stabilization effected by such colloids is called structural-mechanical. For example, humic substances are protective colloids toward hydroxides.

*Molecular colloids* are homogeneous one-phase lyophilic systems, stable and reversible, formed spontaneously. Their particles consist of separate solvate macromolecules. These disperse systems are formed from natural or synthetic high-molecular substances of molecular mass from 10,000 to several millions. The molecules of these substances are of the size of colloidal particles and their true solutions are taken to be colloidal systems. High-molecular colloidal systems are formed in the process of swelling, during which the molecules of the dispersion medium penetrate the solid polymer to expand the macromolecules. With infinite swelling the polymer passes into the soluble state and forms a homogeneous system.

In contrast to the suspensoid particle, the macromolecule can significantly change its shape. Despite the homogeneity of the molecular colloids they are similar to suspensoids in some of their properties (for example, diffusion of light, etc.). The similarity of suspensoids and molecular colloids extends beyond their particle size. Solutions of high-molecular compounds can easily be turned into heterogeneous systems by changing, even insignificantly, the composition of the dispersion medium. For example, protein dissolved in water turns into a lyophobic sol when alcohol is added.

It follows that the molecular colloids are similar to true solutions on the one hand and to suspensoids on the other.

It should be noted that the classification of colloidal systems just described is no more than a matter of convenience, since it is impossible in fact to draw a distinct line between suspensoids and molecular colloids. For example, the interaction between suspensoid particles often produces a gel with properties similar to high-molecular jellies. Moreover, there are many high-molecular inorganic compounds

among mineral substances; for example, a colloidal particle of aluminosilicate can be considered as a macromolecule.

A special group of colloids goes by the name of *micelles*. These are formed from organic long-chain molecules with diphillic properties, i.e. a nonpolar radical reacts better with organic (nonpolar) liquids, while the polar part of the molecule (carboxyl or other groups) reacts better with the polar molecules of water. Micelles are formed by the forces of intermolecular dispersion which become manifest on contact of the nonpolar parts of the molecule. The formation of such colloids is characteristic of aqueous sols of detergents (for example, soap,  $C_{17}H_{35}COONa$ ) and some organic dyes with large molecules. This group also includes synthetic surface-active substances.

Hence different colloidal particles consist of a greatly varying numbers of molecules. For example, each colloidal particle in a colloidal solution of gold consists of dozens, hundreds, and even millions of atoms. Each particle of soap in water contains about 50 molecules, while a colloidal particle of a high-molecular protein compound can consist of only one molecule.

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## 6.2. Preparing Colloidal Systems

The essential precondition for preparing a colloidal solution of any substance is its practical insolubility in a given solvent.

There are dispersion and condensation methods of preparing colloidal solutions.

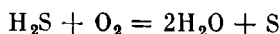
**Dispersion Methods.** These are differentiated according to the method by which particles are reduced in size. The substance can be processed on colloid mills or by electrodispersion.

The substance is processed on a colloid mill to reduce the particle size to that of colloidal particles. Colloid mills are used in the pharmaceutical and food-processing industries. This method is used to prepare some paints and colloidal graphite (a small addition of colloidal graphite to water decreases the deposits of scale in boilers).

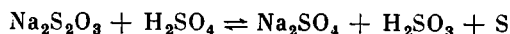
The electrodispersion method is used to disperse metals. Anelectric arc is created between two wire electrodes of the desired metal immersed in water. The electric arc disperses the metal in the liquid medium. A small amount of alkali is added to the water to stabilize the sol obtained. The metal is vapourized and, owing to the low temperature of the water, is condensed to form a sol. This method is used to prepare sols of gold, silver, platinum and of other metals.

**Condensation Methods.** These are based on chemical reactions by which practically insoluble substances are formed. Examples of such reactions are the oxidation of hydrogen sulphide (sulphur is

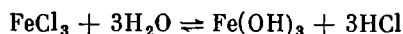
liberated in the colloidal form):



the reaction of sodium thiosulphate with sulphuric acid (with liberation of colloidal sulphur):



the hydrolysis of ferric chloride in hot water (ferric hydroxide is liberated in the free state):



Colloidal solutions can also be obtained by substituting the solvents. For example, if an alcoholic solution of essential oils is mixed with water, a colloidal system of essential oils in water is formed. Essential oils form a true solution with alcohol, but when water is added, it reacts with the alcohol to 'tear' it from the oils. Being insoluble in water, the essential oils form a colloidal solution with it.

Hydrosols are formed spontaneously in natural water or effluents. Humic substances, iron compounds, and other water-insoluble substances pass into natural water from the soil. Hydrosols are formed during the washing of industrial equipment, during transportation of effluents through the waste disposal system, during the contact of currents with rotating surfaces, during the mixing of effluents of different composition, etc.

## 6.3. The Properties of Colloidal Systems

1. Colloids are heterogeneous systems consisting of at least two phases. In this they differ from true solutions which are one-phase, homogeneous systems.

2. Colloidal systems occupy an intermediate position between suspensions and true solutions. They differ from suspensions in that the suspended particles do not settle to the bottom of the vessel on standing, as is the case with suspensions, and from true solutions in that they pass through filter paper but are retained by special membranes of collodion or bovine bladder. Dissolved matter passes through such membranes. This principle underlies the separation of colloids and crystalloids.

**The Molecular and Kinetic Properties of Colloidal Systems.** Like the molecules of a true solution, the colloidal particles of sols are in a state of incessant chaotic motion (Fig. 6.2). The intensity of this movement quickly decreases with growing particle size. The continuous movement precludes the settling of particles and is one of the causes of the stability of colloidal systems. The random move-

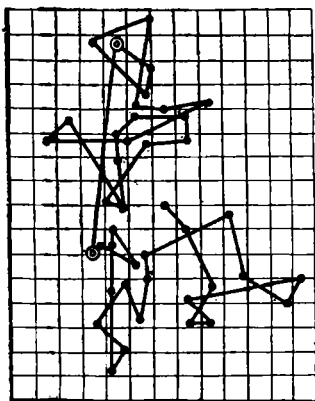


Fig. 6.2. Brownian movement

ment of the colloidal particles is called *Brownian movement*, named after its discoverer, R. Brown. The cause of the visible movement of the colloidal particles is the invisible movement of the solvent molecules which collide with the colloidal particles.

Since the colloidal particles are characterized by thermal motion, the phenomenon of diffusion is also characteristic of them. The connection between the mean displacement of a particle  $\bar{\Delta}$  during the time  $\tau$  and the coefficient of diffusion was established theoretically by Einstein and expressed by the following formula:  $\bar{\Delta} = \sqrt{2D\tau}$ , where  $D$  is the coefficient of diffusion. The latter equals

the amount of the substance passing through a section of one square centimetre per second, when the difference in concentrations, at a distance of 1 cm, is unity:

$$D = \frac{RT}{6\pi r\eta N}$$

where  $R$  is the universal gas constant;  $T$  is the temperature of the system, K;  $r$  is the radius of the particle,  $\eta$  is the viscosity of the medium; and  $N$  is the Avogadro number. The radius of suspended particles  $r$  and the molecular mass of the distributed substances with different dispersities can be determined from  $D$  ( $\text{sq.cm} \times \text{sec}^{-1}$ ). In order to find  $D$ , first the rate of change in the concentration in a given layer should be determined (by the change in refractive index, light absorption, and by other methods).

The osmotic pressure of a colloidal solution is negligibly small compared with that of a true solution. If equal amounts of a substance are used to prepare a true and a colloidal solution, the number of particles of the substance in the true solution will be greater than in the colloidal solution, because the colloidal particles are larger.

Let us calculate the concentration of a disperse system, that is, the number of particles in a unit volume (particle concentration  $v$ , and also gram-particle concentration  $c_g$ , which are interrelated by the equation  $c_g = v/N$ , where  $N$  is the Avogadro number).

**Example.** Determine the gram-particle concentration of 0.1% sol of gold with a particle size of  $l = 10^{-6}$  cm, assuming the particles to be of cubic configuration,  $d = 20$  g/cc.

*Solution.*

1. The volume of the particle,  $v = l^3 = 1 \times 10^{-18}$  cc;
2.  $m = vd = 1 \times 10^{-18} \times 20 = 2 \times 10^{-17}$  g;

3. 1 litre contains (the density of the gold sol being unity)  $0.1 \times 10 = 1$ ; then

$$c_g = \frac{1}{2 \times 10^{-17} \times 6.02 \times 10^{23}} = 1 \times 10^{-7} \text{ gram-particles/litre}$$

Hence, the gram-particle concentration is about 7 orders smaller than the molecular concentration. This accounts for the insignificant osmotic pressure in colloidal solutions.

The colloidal particles are distributed in the colloidal system in a specific manner (Fig. 6.3). The concentration of the disperse phase in the lower layers of the solution is significantly higher than in the upper layers. The regularities of the distribution of colloidal particles in the dispersion medium were formulated by Perrin (*sedimentation equilibrium*). The way in which the colloidal particles are distributed in the vertical plane of the solution is very much like that of gases in the atmosphere. If a colloidal system with such a particle distribution, in a state of equilibrium, is jolted or otherwise agitated, it returns to the initial state after a certain period of time. The time during which a sedimentation equilibrium in a colloidal system is attained is rather short (measured in days), but the equilibrium then persists for an indefinitely long period.

The kinetic stability of a colloidal system is characterized by the hypsometric law, which, when applied to the colloidal system, has the following expression

$$h = \frac{RT \ln \frac{n_1}{n_2}}{Nmg} \left( \frac{v}{v - v_0} \right)$$

where  $h$  is the height of the layer in which the particle concentration changes from  $n_1$  to  $n_2$ ;  $N$  is the Avogadro number;  $m$  is the mass of the particle;  $g$  is the gravity force;  $v$  is the density of the disperse phase; and  $v_0$  is the density of the dispersion medium. This equation can be used to determine the micellar mass of the dispersed substance.

**The Optical Properties of Colloidal Systems.** A colloidal system is characterized by optical nonuniformity. The colloidal particles can scatter a beam of light in all directions. The path of a light beam passing through a colloidal solution, as viewed from the side, appears in the form of a band of light, just like a light beam passing into a dark room through a hole in the shutter. This phenomenon is known as the *Tyndall effect* (Fig. 6.4). The Tyndall effect is used to distinguish colloidal solutions from true solutions, since the latter are "optically clear", because their small particles do not scatter light.

The optical properties of disperse systems are used to study their structure, to determine the dimensions and shapes of particles and their concentration. All these determinations are based on the commensurability of electromagnetic light wave and the size of the

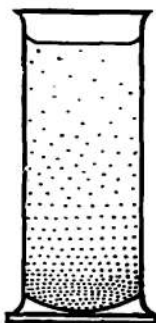


Fig. 6.3. Sedimentation equilibrium

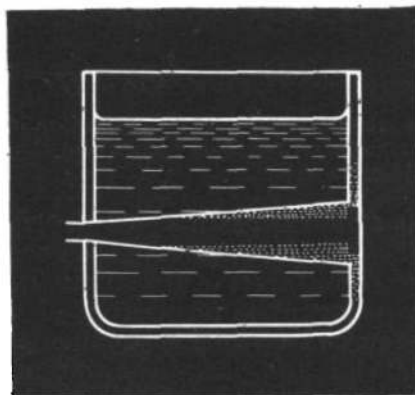
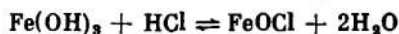


Fig. 6.4. Tyndall effect

colloidal particles. Since the colloidal particles are appreciably smaller than the wavelength, they scatter light due to its diffraction in a microheterogeneous disperse system.

## 6.4. The Structure of a Colloidal Particle

**The Electrical Double Layer.** A suspensoid particle (micelle) has a composite structure. The centre is a nucleus insoluble in a given medium. As a rule, the nucleus is a microcrystal or an aggregation of microcrystals. The surface of the nucleus adsorbs ions from the surrounding medium through the action of free interface energy, in accordance with Fajans' rule.\* These ions are *potential-forming* ions, since they give a charge to the particle. As the ions are adsorbed, the interface free energy decreases and the system is stabilized. For example, a potential-forming ion for the sol of ferric hydroxide is iron oxychloride, which is formed according to the equation



The oxychloride dissociates according to the equation



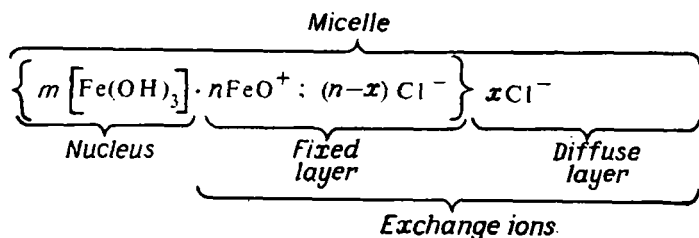
The cation  $\text{FeO}^+$  is adsorbed selectively on the surface of the colloidal nucleus to give it a positive charge. If  $n$  number of  $\text{FeO}^+$  ions

\* Fajans' rule is as follows: the surface of the nucleus of a lyophobic micelle adsorbs mainly those ions which have common chemical elements with the nucleus or which are characterized by isomorphism with the crystalline lattice of the nucleus.

have adsorbed, the solution contains  $n$   $\text{Cl}^-$  ions. The cation  $\text{FeO}^+$  gives a positive charge to the colloidal particle, while its counterions are the chloride ions in the solution. The counterions are acted upon by two forces: the electrostatic force which attracts them to the nucleus of the colloidal particle, and the diffusion force which tends to scatter them in the solution. As these two forces exert their influence, the state of separate chloride ions is different. Some of them bind tightly to the nucleus of the colloidal particle to form a fixed *adsorption layer* ( $n - x$ ), while others form the *diffuse layer*  $x$ , the ionic atmosphere of the particle.

The combination of the diffuse and the adsorption layers is the *electrical double layer*.

The ions of the diffuse layer continuously exchange with like ions in the fixed layer and are therefore called *exchange* ions. The nucleus and the fixed layer form a *granule*, while the system containing the granule and the diffuse layer is called a *micelle*.



A ferric hydroxide micelle is shown schematically in Fig. 6.5.

Figure 6.6 shows the structure of an electric double layer of fixed and diffuse structure.

The potentials of the solid particle and the liquid are compensated in the fixed layer; while in the diffusion structure, which is characteristic of liquids, the potential of the solid particle is compensated only partially, since only a proportion of the counterions are held near the solid particle in the fixed layer of the liquid.

The difference in potentials which arises at the interface between the mobile and the fixed layer is known as the *electrokinetic potential* and is designated by the Greek letter zeta ( $\zeta$ ), hence its alternative name *zetapotential*. Hence the electrokinetic, or zeta, potential is the difference in potentials at the interface between the fixed (adsorption) layer of a liquid and the mobile (diffuse) layer.

The total fall in potential at the interface between the solid and solvent ( $NM$ ) to zero reading  $C$  (Fig. 6.7) corresponds to the maximum difference of potentials of the solid and all counterions taken together. This maximum potential difference is called the *thermodynamic potential* and is designated by the letter  $\epsilon$ . This potential corresponds to the case illustrated in Fig. 6.6a.

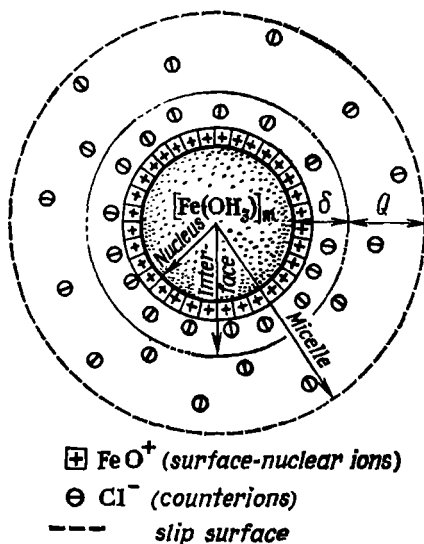


Fig. 6.5. The structure of a ferric hydroxide micelle:

$\delta$ —fixed layer;  $Q$ —diffuse layer of counterions

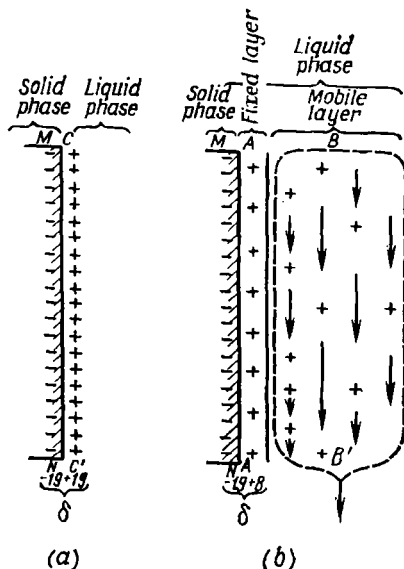


Fig. 6.6. The structure of a double electric layer:

$a$ —fixed layer;  $b$ —diffuse structure of the layer

The thermodynamic and electrokinetic potentials differ from each other. They arise in different parts of the system: the former at the interface between the solid surface and liquid, and the latter at the interface between the mobile and the fixed layers of the liquid.

The thermodynamic potential gives the maximum difference of potentials between all positive and negative charges, while the electrokinetic potential is only part of this difference. Figure 6.7 shows that

$$\zeta = \varepsilon - \varepsilon_1$$

where  $\zeta$  is the electrokinetic potential;  $\varepsilon$  is the thermodynamic potential;  $\varepsilon_1$  is the drop in the potential in the fixed layer caused by the compensation of the charges on the solid particle by the 'bound' counterions.

To compare the thermodynamic potential with the electrokinetic, let us calculate on the basis of the data given in Fig. 6.7. Assume that the minus sign on the figure corresponds to a charge  $-1$ , while the plus sign to a charge  $+1$ . Then, the charge of the solid surface will be  $-19$ , and the overall charge of the counterions,  $+19$ . The potential difference, corresponding to the thermodynamic potential, is

$$\varepsilon = (+19) - (-19) = 38$$

(layer  $\delta$ , see Fig. 6.6a).

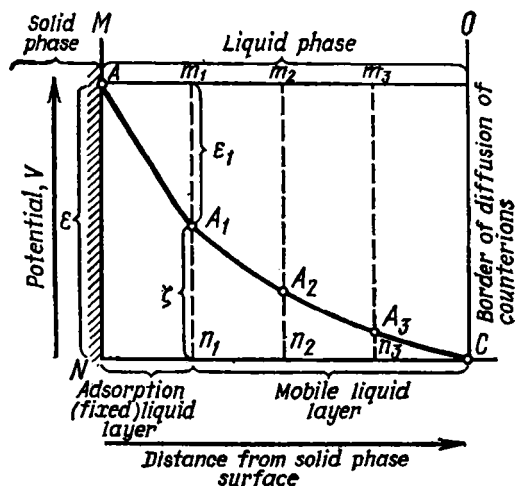


Fig. 6.7. Comparison of the thermodynamic  $\epsilon$  and electrokinetic potentials (zeta potential)

The fixed double layer (see Fig. 6.6b) bears the charges:  $-19$  (the solid particle) and  $+8$  (in the adsorption layer). The overall charge on the fixed double layer is then

$$(+8) + (-19) = -11$$

The potential difference, corresponding to the zeta potential is  $\zeta = (+11) - (-11) = 22$ . Hence the electrokinetic potential is always smaller than and a part of the thermodynamic potential.

The magnitude and sign of the zeta potential are determined from the electrophoresis or electroosmosis data and also from the streaming potential. The zeta potential is of the order of 50-70 mV.

The zeta potential is of great practical importance in the purification of water. For example, during the destruction of disperse systems with coagulating agents, the zeta potential decreases to the critical point, i.e. to the isoelectric point of the colloidal particle, corresponding to the maximum speed of the coagulation process. It follows therefore that the coagulation with electrolytes results from the compression of the diffuse layer (see Fig. 6.6a) at the expense of the increasing concentration of counterions in the diffuse layer. Once the diffuse layer is compressed to  $CC'$  (see Fig. 6.6a), the zeta potential becomes zero.

Thus the zeta potential is a measure of stability of a colloidal system. When it decreases, the stability decreases as well, although this holds only for sols of low concentration.

The dependence of the zeta potential on the concentration is complicated in solutions of potential-determining ions. Excess ions in

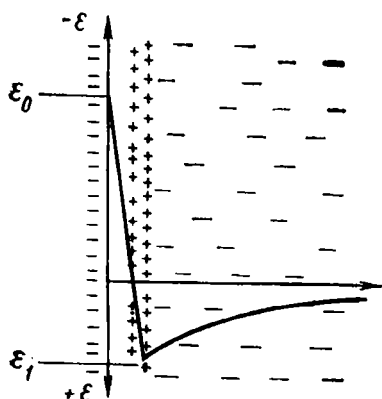


Fig. 6.8. Ion distribution and the potential drop in the electrical double layer in extra-equivalent adsorption

the medium can alter the charges and potentials in the electrical double layer. The potentials may be changed by the specific adsorption according to Fajans' rule. For this reason, the zeta potential decreases with the growing concentration of the ions until the isoelectric point is overcome, then it changes the sign of the charge and increases again to a certain limit. Curves showing the dependence of the zeta potential on pH have been obtained for amphoteric substances ( $\text{Al}_2\text{O}_3$ , proteins, etc.).

The signs of  $\varepsilon$  and  $\zeta$  can change because of the extraequivalent (specific) adsorption of counterions in the adsorption layer under the influence of additional non-Coulomb (van der Waals) forces.

This can be seen either with the ions that polarize the solid phase (e.g. polyvalent ions  $\text{Ce}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ) or complex organic ions (alkaloids, surfactants, dyes) polarized by the solid phase. The electrical double layer thus becomes a three-layer structure (Fig. 6.8).

According to the theory of the electrical double layer, the potential drop in the fixed layer (line  $AA_1$ , Fig. 6.7) obeys the linear law (in accordance with the theory of a parallel plate capacitor), while in the diffuse layer this linearity is absent: the potential decreases according to the exponential law (see Fig. 6.7, curve  $A_1C$ ).

## 6.5. Electrokinetic Phenomena

The charge on a colloidal particle is detected as follows. Two electrodes connected to the poles of a current source are immersed in a sol. The voltage across the electrodes is sufficiently high. As direct current is passed through the solution, the colloidal particles slowly move toward one of the electrodes. This phenomenon was observed by the Russian scientist Reuss in 1807. He plunged two glass tubes *A* and *C* (Fig. 6.9) into a bed of moist clay to make two cylinders with clay bottoms. Next he put well-washed sand into the cylinders and added water to the same level in each. Electrodes were then inserted into the cylinders and connected to a current source. The liquid in the cylinder *A* (containing the positive electrode, or anode) then became turbid because the particles of clay moved up from the bot-

tom and formed a suspension in the water. The level of liquid in the anode cylinder A dropped and was raised in the cathode cylinder C.

The movement of the colloidal particles under the influence of an electric field indicates that they carry an electric charge.

As an electric current passes through a colloidal system, coarse colloidal particles (granules) move toward one electrode and the counterions toward the other.

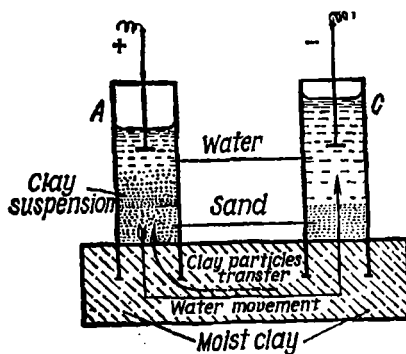


Fig. 6.9. Reuss' experiment

The migration of dispersed particles under the influence of an electric field is called *electrophoresis*. Electrophoresis differs from electrolysis in that electrolytic processes obey Faraday's law, i.e. the amounts of the substances deposited at the electrodes are proportional to their equivalent weights. This proportionality is absent in electrophoresis: the formation of a colloidal particle is not connected with the chemical equivalent of a given substance.

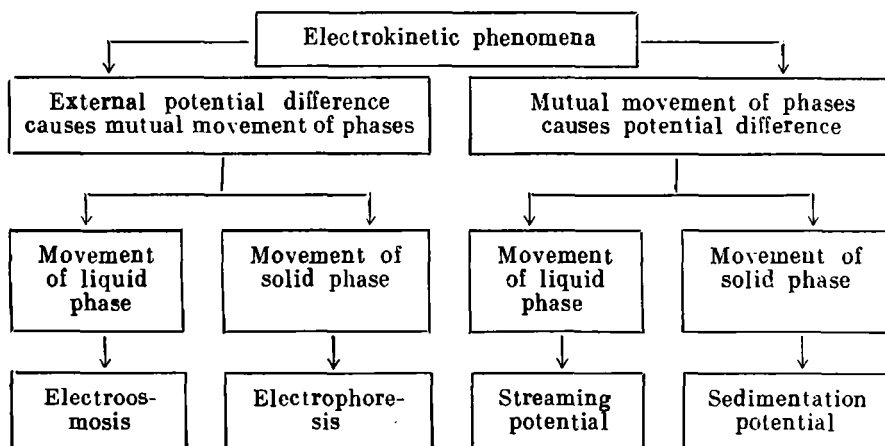
The movement of liquid through a porous body under the influence of the external potential difference is called *electroosmosis*. Electroosmosis occurs not only when a liquid passes through clay but also through porous diaphragms prepared from other materials (porcelain, glass or quartz powder, frozen or dense soil, etc.).

In Reuss' experiment, the liquid and solid phases migrate under the influence of an external electric field. Later phenomena the reverse of electroosmosis and electrophoresis were discovered. If a liquid passes through a capillary under pressure, a potential difference is formed at the ends of the capillary, this difference interfering with the passage of the liquid. These are *streaming potentials*. They arise on the opposing walls of porous diaphragms if a liquid is passed through them under pressure. This phenomenon is the reverse of electroosmosis.

If solid particles quickly precipitate to the bottom, a potential difference between the superficial layer and the layer adjacent to the bottom arises. This is termed the *sedimentation potential*, which is the reverse of electrophoresis.

The mutual movement of the solid and liquid phases which arises due to the potential difference is called *electrokinetics*. For the sake of clarity, the electrokinetic phenomena are shown in the following

diagrammatic form:



## 6.6. The Causes of the Stability of Colloidal Systems

The stability of a colloidal system depends on three factors, electrical, structural-mechanical, and kinetic.

As has already been said, the stability of a colloidal system strongly depends on the presence of a stabilizing agent, the substance of the ionic or molecular structure which is adsorbed on the particle nucleus. Where there is an ionic stabilizer electrical double layers are formed around the micelle nucleus. These layers prevent micellar aggregation (the *electrical factor*).

If the stabilizer has a molecular structure, the ionic layers do not form, but, due to the action of the intermolecular forces, solvate sheaths (layers) consisting of molecules of the dispersion medium are formed on the adsorbed molecules to preclude aggregation.

Unstable sols of hydrophobic colloids, which easily coagulate, can be rendered stable against the action of electrolytes if small amounts of any hydrophilic colloid (e.g. gelatin, gum arabic, humins, etc.) are added. Hydrophilic colloids produce the *protective* action on suspensions as well. Suspension particles settle very slowly in the presence of such colloids. In nature, the role of the protective colloids is played by humins, which are effective for hydroxides of iron and aluminium.

The protective mechanism is based on hydrophilic substances being adsorbed on the surface of hydrophobic particles to form hyd-

rate sheaths around the particles at the expense of van der Waals forces, hydrogen and coordination bonds. B. V. Derjaguin showed that these layers prevent the attraction of particles and, in order to overcome the resistance, work must be performed.

The minimum quantity of a hydrophilic substance that can stabilize a hydrophobic colloid is given the name of the colloid which it protects, viz., gold number, silver number, congorubin number, etc. The sol numbers are the inverse measure of the protective action: they become lower the greater the strength of their action.

The sol numbers depend on the nature of the high-molecular compounds and colloidal systems. For example, the protective action of casein toward hydrosol of gold is 2500 times stronger than that of starch, while the protective action of casein toward the sol of congorubin is only 50 times stronger than that of starch.

Surface active substances produce the same protective action on hydrophobic colloids. But the character of surfactant orientation in the adsorption layer becomes of great importance. The stability of colloidal systems in an aqueous medium is higher if the polar groups of the surfactants of the adsorption layer are directed into the water, since it is only on this condition that the hydrophilic properties of the surface are improved. It has been established that adsorption layers are not always uniform. In many cases, a system is stabilized if only 40-60 per cent of the surface of the colloidal particles are covered with the unimolecular layer, the protective layer then not being continuous. But the maximum stability of some colloidal systems depends on the formation of a complete unimolecular layer (for example, after adding gelatin to gold sols or quartz suspensions).

The layers with adsorbed molecules of surfactants have resilience and mechanical strength which prevents coagulation of the dispersed particles. The formation of molecular-adsorption rigid-like layers is called the *structural-mechanical stabilization factor* (P. V. Rebinder).

The *kinetic factor* in colloidal system stabilization manifests itself in the mean kinetic energy of the translatory motion (heat motion) of particles of the disperse phase and in the mean free surface energy.

The growing mean kinetic energy of the system results in kinetic stability (stability against the settling of particles). The growing free surface energy per particle of the disperse system decreases the aggregative stability (stability against sticking of particles).

The rising temperature of the colloidal system produces a dual effect on the stability of a system. It increases the kinetic and decreases the aggregative stability. As the kinetic energy of the translatory motion of particles increases, the particles approach one another to a point at which the intermolecular forces of attraction become effective and the particles are thus enlarged.

The factor which increases the stability of a system is *dissolution*, the process during which the size of the particles gradually diminishes.

Insignificant difference in the density and viscosity of the disperse phase and the dispersion medium stabilizes a disperse system. In these conditions, the random movement of particles prevails over the force of gravity, and the kinetic stability increases.

## 6.7. Destruction of Disperse Systems

A system of bodies is in a state of stable equilibrium when the free energy is as low as possible. The high interface free energy in colloidal systems due to the developed interface accounts for the low stability of these systems.

An unstable system can break down if the external conditions are altered, for example, the system is heated, frozen, or acted upon by electromagnetic fields, hard rays or exposed to mechanical or chemical action. These external factors enlarge the size of the particles. The coarsening of the colloidal particles, which decreases the dispersivity of the disperse phase, is called *coagulation*.

Natural waters and effluents are separated from colloids mostly by the chemical coagulation method which entails adding an electrolyte to the system.

**The Coagulating Action of an Electrolyte.** All electrolytes produce coagulation. A substance coagulating the disperse phase of a colloidal system is called a *coagulant*, while the ion which initiates the process is called the *coagulating ion*.

The addition of an electrolyte to a solution strongly increases the overall concentration of the ions and this produces favourable conditions for absorption by the charged colloidal particles of the oppositely charged ions. The initial charge on the particle thus decreases to the critical value and the sol coagulates. This is the explanation that electrostatic theory gives to the coagulation mechanism. B. V. Derjaguin treats the coagulation process in a different way. According to his physical theory, a liquid film forms between two solid particles in a sol. This film holds the particles apart to prevent their attraction. The wedging action of the film increases strongly with the thinning of the film and depends heavily on the presence of electrolytes. When an electrolyte is added to a disperse system, the strength of the separating film is impaired and the stability of the sol is upset. At the moment the colloidal particles coagulate, the distance between them must be such that the energy of their mutual attraction (due to the van der Waals forces) is greater than the energy of heat (Brownian) movement. But the forces of electrostatic repulsion which arise between the electrical double layers prevent the colloidal particles getting close enough to each other. Derjaguin has proved that the forces of electrostatic repulsion arise only when the ionic atmospheres of the colloidal particles overlap (Fig. 6.10). At

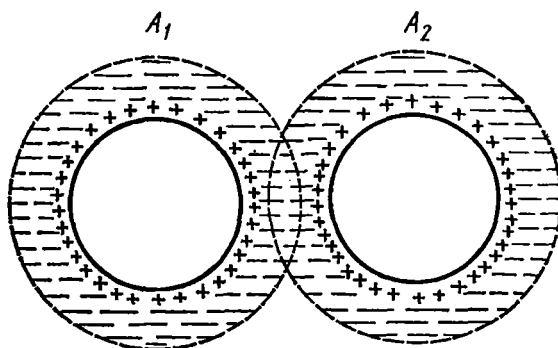


Fig. 6.10. Overlapping of the ionic atmospheres of two colloidal particles (after Derjaguin)

this point the ions are redistributed according to the local changes in their concentration, owing to which additional electrostatic forces arise which cause the mutual repulsion of the colloidal particles.

The energy of the interaction between two colloidal particles which depends on the distance between their surfaces is expressed by the potential curves obtained by summing the forces of inter-particle attraction and electrostatic repulsion. Figure 6.11 shows potential curves describing the interaction of two colloidal particles. Curve *I* has the energy barrier (*S*). This barrier develops at a distance  $r_0$  between the particles and the repulsion forces prevent them becoming closer. If the concentration of the electrolyte (coagulant) is sufficiently high, the diffuse layer is compressed and the particles move to a distance  $r_2$  from each other, which is less than their radii. The attraction force becomes effective at this distance and the particles begin to coagulate thus lowering the dispersity of the system.

**Flocculation Value.** The minimum quantity of electrolyte which causes flocculation is known as the flocculation value  $\gamma$ ; it is expressed in millimoles/litre and corresponds to the compression of the electrical double layer to the point that it can no longer serve as an energy barrier holding the particles from sticking together.

Hardy found in 1900 that the coagulating action in the electrolyte applies only to those ions whose charge is the same as that of the counterion of the colloidal particle.

*The coagulating action of these coagulating ions depends on their valency: the higher the valency the stronger the coagulating action of the ions (Schulze-Hardy rule).*

The Schulze-Hardy rule was verified and theoretically substantiated by Derjaguin and Landau. The theory provides the following formula for the flocculation value:

$$\gamma = C \frac{\epsilon^3 (kT)^5}{A^2 e^6 z^6}$$

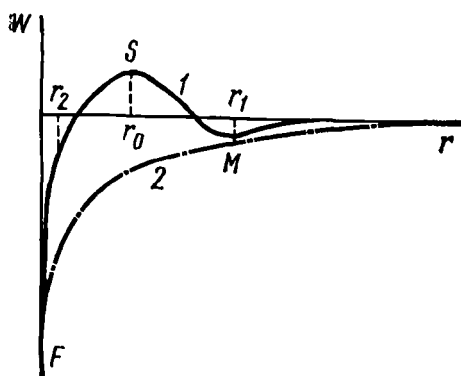


Fig. 6.11. Energy of interaction of two colloidal particles depending on the distance between their surfaces:

1—stable systems; 2—unstable systems

where  $C$  is a constant dependent on the ratio of the charges on the cation and the anion;  $e$  is the charge on the electron;  $k$  is the Boltzmann constant\*;  $A$  is the constant of the van der Waals attraction;  $\epsilon$  is the dielectric constant of the medium, and  $z$  is the valency of the coagulating ion.

It follows from the equation that the flocculation values for uni-, di-, ter-, and tetra-valent ions are related as follows:

$$\gamma = 1 : \left(\frac{1}{2}\right)^6 : \left(\frac{1}{3}\right)^6 : \left(\frac{1}{4}\right)^6$$

or  $1 : 0.016 : 0.0013 : 0.00024$ . But the flocculation value is a relative characteristic of stability of the sol with respect to a given electrolyte, since it depends on the nature of the coagulated sol and the coagulating ion, as well as the concentration of the sol. The formula shows that the flocculation (concentration) value does not depend on the potential of the particle surface, but depends on the van der Waals constant  $A$ , on the dielectric constant of the system  $\epsilon$ , and on the temperature and valency of the coagulating ion. The partner ion produces a negligible effect on coagulation, only changing the coefficient  $C$  slightly.

A special case of coagulation by electrolytes is the mutual coagulation of two hydrophobic colloids with unlike charges. The overlapping of the ionic atmospheres here promotes the attraction of the colloidal particles. The distance between particles at which mutual coagulation occurs is many times greater than the radii of the particles. The most complete coagulation occurs during mutual neutralization of the charges on the particles. If one sol is taken in excess, the ions can be redistributed and modified double layers formed around the particles. The system on the whole can be stable and bear a charge with the sign of the colloid in excess.

The chemical processes involving electrolytes of the inter-particle fluid, with subsequent shift of the adsorption equilibrium, and also the processes between the electrolytes and the colloidal particles, are of prime importance in the interaction of various hydro-sols with particles of like charge.

When a sol is coagulated by a mixture of two electrolytes, three outcomes are likely:

\* Universal gas constant applied to one particle.

1. *The additive action of the electrolytes.* The coagulating action of each manifests itself irrespective of the other, and the overall effect therefore depends on the sum of the concentrations of the substances added to the system. This phenomenon occurs with electrolytes with similar coagulating properties.

2. *Antagonism of electrolytes.* In this case, the number of coagulating ions required for coagulation is greater than for the additive action of the electrolytes. The elevated flocculation value which is found with the mixing of electrolytes is called *antagonism of ions*. This is the competition of the ions for the adsorption centres on the surfaces of the colloidal particles. The antagonism manifests itself between ions with significant differences in coagulating action, for example, the antagonism between  $\text{Al}^{3+}$  and  $\text{K}^+$  in the coagulation of the negative sol of  $\text{AgI}$ .

3. *Synergism of electrolytes.* The electrolytes intensify each other's action and the amounts required for coagulation are therefore smaller than with the additivity case.

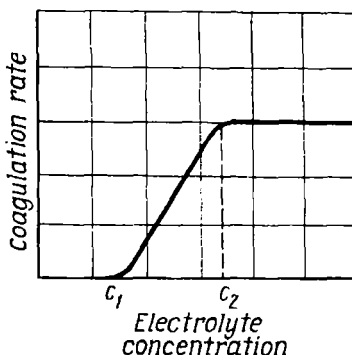


Fig. 6.12. Coagulation curve

**Coagulation rate.** The dependence of the coagulation rate of a colloidal solution on the concentration of the electrolyte is shown in Fig. 6.12. If the electrolyte concentration is low coagulation does not occur, since the adsorption of the oppositely charged ions is insignificant and the colloidal particles bear a sufficient like charge to prevent their coagulation. The charge decreases with time and the force of attraction between the particles becomes effective.

Coagulation by electrolytes with concentrations varying from  $c_1$  to  $c_2$  is a *slow process*. If the concentration of the electrolyte is  $c_2$ , the charge on the colloidal particles becomes zero. The coagulation rate at this point is at a maximum, and the further addition of electrolyte can change the sign of the charge on the colloidal particles.

*Rapid coagulation* processes obey the second order kinetic law:

$$-\frac{dc}{d\tau} = kc^2$$

Integration gives

$$k = \frac{1}{\tau} \left( \frac{1}{c} - \frac{1}{c_0} \right)$$

where  $c_0$  is the number of particles contained in unit volume before coagulation,  $c$  is the number of particles in the same volume after coagulation at the moment of time  $\tau$ ;  $k$  is the coagulation rate constant. The time during which half of the suspended particles is

coagulated  $\left(\frac{c_0}{2}\right)$  is

$$\tau_{1/2} = \frac{1}{kc_0}$$

The criterion for slow coagulation, continuing for hours, is the coagulation rate constant  $k$ . This is determined experimentally and compared with the theoretical constant calculated from the equation

$$k = \frac{4RT}{3\eta N_A}$$

where  $\eta$  is viscosity of the medium;  $N_A$  is the Avogadro number. If the experimental  $k$  is smaller than the theoretical, this indicates that a slow coagulation process is occurring in the system. If coagulation is rapid lasting for a fraction of a second, the experimental and theoretical constants should be equal.

**The Coagulation of Colloidal Systems by the Action of Physical Factors.** Coagulation through mechanical factors occurs during the mechanical stirring of colloidal systems, their pumping through pipes, etc. Coagulation in such cases is explained by the temporary upsetting of the adsorption equilibrium of the stabilizing agent on the surface of the colloidal particles. This promotes the movement of the particles toward one another to a distance where the van der Waals forces become effective. This is confirmed by the fact that the coagulate (coagulated sol) obtained by mechanical coagulation always contains smaller quantities of the stabilizer than the coagulate obtained by the action of electrolytes.

Coagulation induced by dilution or concentration of sols can be explained by desorption of the stabilizing electrolyte from the particle surface which accounts for the drop of the charge on particles. This can cause hydrolysis in the system with reduction of its stability.

If a colloidal system is diluted with technical water containing electrolytes, the system can coagulate as well. During the evaporation process, the sol becomes more concentrated and this renders the system unstable.

Coagulation by heating is explained by the intensified Brownian movement which causes desorption of the stabilizing agent from the colloidal particle, while the destruction of the electrical double layer lowers the energy barrier between the particles, causing their sticking together.

If a system is frozen by the Luttermoser method, hydrosols are coagulated by freezing out the water from the disperse phase. The coagulation is facilitated if the whole bulk of the sol is frozen. The frozen system expands and high pressure develops in it. The compressed particles of the disperse phase contact each other and coagulate.

A. V. Dumansky has suggested that crystals of pure water are formed during freezing of the sol, and that the concentrations of the sol and the electrolyte gradually increase in the remaining liquid. When the electrolyte concentration becomes high the system coagulates.

Zsigmondy established that the stability of a disperse colloidal system is greater if the system is stable with regard to the action of electrolytes or the removal of water by drying. Hence, the degradation of a sol on standing or when subjected to physical factors such as stirring, frost, heat, light, electric discharge, ultrasound, etc., entails the destruction of the electrical double layer around the colloidal particle.

Figure 6.11 shows a potential curve (1), on which, at a distance  $r_1$  between particles, there is minimum  $M$ . For hydrophobic sols its position is insignificant, but for relatively large asymmetrical particles in the form of rods or platelets the energy of interaction at point  $M$  exceeds the energy of heat motion and the particles attract one another at a considerable distance (of the order of several thicknesses of the electrical double layer). This promotes the formation of a gel which is unstable and readily destroyed by shaking. The isothermic gel-sol transformation is known as *thixotropy*. Thixotropic structures arise only with certain concentrations of colloidal particles and electrolytes. The quantitative characteristics of thixotropy are determined by measuring the kinetics of spontaneous restoration of mechanical properties (modulus of shear elasticity, strength, etc.), depending on the time for which the system is allowed to rest.

To coagulate hydrophilic colloids, greater amounts of electrolyte are required than to coagulate hydrophobic colloids. The coagulation of hydrophilic colloids is called *salting out* (e.g. salting out of soap from an alkaline solution). The main role in this process belongs to the destruction of the hydrate sheath of the particle, the role of the charge on the particle being only secondary. Figure 6.13 shows the coagulation diagram for hydrophilic and hydrophobic sols.

As hydrophilic colloids precipitate, they entrap the liquid phase (sometimes the entire solvent), to form a jelly. Such precipitates are called *gels*. The process of transformation of a sol into a gel is called *gelation*. A gel can be converted back to a sol by heating. When allowed to stand, a jelly undergoes great changes. It shrinks to liberate

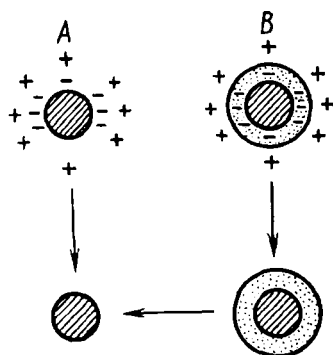


Fig. 6.13. Coagulation with an electrolyte:

A—hydrophobic particle; B—hydrophilic particle

the solvent. This phenomenon is called *syneresis*, or the ageing of a gel.

**Gels and Jellies.** Gels are structures formed by colloidal particles or molecules of polymers in the form of simple three-dimensional lattices whose cells are filled with the dispersion medium. One should distinguish between rigid and elastic gels. Silica gel,  $\text{H}_2\text{SiO}_3$ , is a rigid gel. Having a rigid framework, it does not change its volume on drying or moistening. A dried rigid gel has a well-developed porous structure with a multitude of rigid capillaries. The formation of rigid gels from lyophobic sols is seen by Rebinder as a kind of structure formation by coagulation. Rigid gels are two-phase heterogeneous systems.

Elastic gels, or jellies, are formed by high-molecular compounds, and in contrast to rigid gels are one-phase systems. The chain flexibility in the three-dimensional lattice accounts for the changes that readily occur in the volume of elastic gels, associated with absorbing or giving off the dispersion medium. Elastic gels can swell to expand their volume dozens of times.

The coagulation is complicated by the reverse process, known as *peptization*\*, by which the coagulate turns into a sol. The process is spontaneous and does not require any external energy to increase the interface. Peptization is more likely to occur in freshly precipitated systems and depends on the lyophilic properties of the precipitated sol. The higher the lyophilic power, the greater the probability of peptization. As time passes, the particles interact to decrease the dispersity of the system and to lower the surface energy. The coagulation in such cases becomes irreversible and the system does not peptize. Peptization can occur if an electrolyte containing potential-forming ions is added to the system. For example, amphoteric coagulates of the type  $\text{Al}(\text{OH})_3$  are peptized by alkalis or acids added in quantities which although small are, however, sufficient to increase the charge on the particle. Sometimes the peptization process can be initiated by washing the precipitate from the electrolyte (concentration coagulation). Despite the obvious difference in the methods (removal of electrolyte and adding of electrolyte) the mechanism of peptization in both cases involves increasing the potential energy of repulsion, which results in peptization.

Hence, coagulation is a reversible process and under certain conditions a dynamic equilibrium is achieved in the system ( $\text{sol} \rightleftharpoons \text{aggregations}$ ) which prevents completion of the process.

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\* Peptization originally meant the digestion of proteins by the enzyme pepsin, but now it generally implies the converse of coagulation because of the apparent similarity of the two processes.

## 6.8. Surface Phenomena

Surface phenomena in heterogenous systems occur at the interface and are of great practical importance. They are connected with the processes of wetting, spilling, flotation, and emulsification, with the detergent properties of some substances, with the crushing of solids, and the chemical and biochemical purification of water, etc.

Surface processes are associated with a decrease in free surface energy.

As molecules approach one another, they become even more attracted by the van der Waals forces\*. These cohesion forces show up in gaseous, liquid and solid bodies. They are greater in solids than in liquids, while the weakest cohesion forces are in gases.

Let us consider the causes of the development of surface energy in a solid substance. The state of the molecules in a solid substance varies and depends on their orientation in the particle. Figure 6.14 shows, by convention, the spheres of molecular action (broken lines). The molecules located inside the particle have no free field of force since the intermolecular forces are fully compensated here. The molecules located at the surface of the particle have surplus field of force because the intermolecular forces in them are compensated only partly (shaded part). The length of the arrows shows the conventional relative magnitude of free surface energy at a given point. Figure 6.14 also shows that the molecules located at the peaks of the uneven surface of a solid substance possess the greatest surplus of free surface energy.

Hence, free surface energy depends on the size and shape of the surface which in turn depends on the size of the particles. If a substance is ground, its specific surface (the surface of a substance as referred to its unit volume) increases (see Table 6.1).

If we grind a cubic centimeter of a substance into a colloidal state, the overall surface of its particles increases from 6 sq.cm to at least 60 sq.m.

The larger the surface of a substance in the colloidal state, the more intense are the surface phenomena, adsorption in the first instance.

By *adsorption* is understood the process by which gases, vapours, and dissolved solids are concentrated on the surface of a substance under the action of free surface energy.

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\* The intermolecular forces comprise the *orientation* force which is the electrostatic interaction of dipole molecules; *electrokinetic* or *dispersion* forces, which arise due to a coordinated movement of electrons in the molecules approaching each other, or fluctuating dipoles (these are known as dispersion forces because the fluctuating dipoles are the cause of light scattering) and *induction* forces which are due to the appearance of induced dipoles at the expense of molecule polarization.

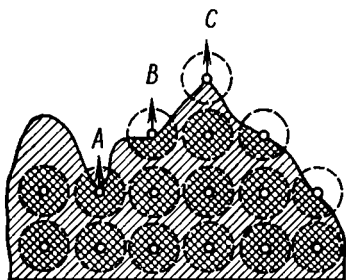


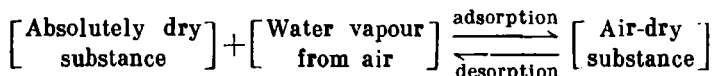
Fig. 6.14. Surface energy of a solid substance

A substance capable of adsorbing other substances on its surface is called an *adsorbent*, while the substance which is adsorbed on it is known as an *adsorbate*.

An adsorbent must possess a free field of force by which the surface layer can attract the particles of the liquid or gaseous phases that come in contact with it. In many cases the adsorbed layer of particles is monomolecular, i.e. has the thickness of one molecule.

The adsorption equilibrium is dynamic. Some adsorbed molecules are torn off the adsorbent and pass into the surrounding medium. This phenomenon, the reverse of adsorption, is called *desorption*. And conversely, the molecules of the surrounding medium precipitate on the adsorbent.

If a dry substance is kept in humid air it will adsorb moisture from the air until an adsorption equilibrium is attained:



The state of adsorption equilibrium depends on both the concentration of the solute adsorbed in the medium in contact with the adsorbent, and the temperature. The increasing concentration of the adsorbate intensifies the adsorption process, while the rising temperature causes desorption, since adsorption is an exothermic process.

The adsorption equilibrium is achieved very quickly, usually in a few seconds, or at the most a few minutes. If the adsorption equilibrium sets in slowly, the adsorption process is combined with some other surface processes (chemisorption or absorption).

The molecules of a gaseous substance or vapour can penetrate (diffuse through) the bulk of the adsorbent to form a uniform mass. The process of the taking up of a substance

Table 6.1

The Increase in the Number of Particles and the Enlargement of Their Summary Surface Area Resulting from the Size Reduction of 1 cc of Substance

Particle length, cm	Number of particles after size reduction	Overall surface area of particles, sq. cm
1	1	6
$10^{-1}$	$10^3$	$6 \times 10$
$10^{-2}$	$10^6$	$6 \times 10^2$
$10^{-3}$	$10^9$	$6 \times 10^3$
$10^{-4}$	$10^{12}$	$6 \times 10^4$
$10^{-5}$	$10^{15}$	$6 \times 10^5$
$10^{-6}$	$10^{18}$	$6 \times 10^6$
$10^{-7}$	$10^{21}$	$6 \times 10^7$

by the entire bulk of the adsorbent is called *absorption*. Hence, absorption is a volumetric phenomenon while adsorption is only superficial. The dissolution of any gas in liquid is an example of absorption.

If the adsorbate reacts chemically with the adsorbent the process is called *chemisorption*\*. Chemisorption can occur both on the surface and throughout the bulk of the adsorbent. For example, the formation of a thin oxidic film on metals (Al, Zn, Mn) which protects them from corrosion is explained by chemisorption. If the chemical compounds that are formed on the surface of the adsorbent are loose, chemisorption can extend to the deeper portions of the adsorbent, as for example, in the corrosion of iron or the absorption of gases in soda lime (a mixture of calcium hydroxide and sodium hydroxide).

All these three phenomena, namely, adsorption, absorption and chemisorption are given the common name *sorption*.

The nature of adsorption has been thoroughly studied by many researchers. It has been established that under various conditions and at various stages of adsorption, both physical and chemical processes of various intensity occur. During adsorption of the first portions of a substance, a chemical process takes place (the shapes of the adsorbate molecules are altered and the bonds in them deformed), while at the subsequent stage, the process becomes a purely physical one. For example, when the first portions of oxygen are adsorbed by carbon, and by many metals, its compounds with the most active sites of the adsorbent surface (Fig. 6.14, point *C*) are formed. If the adsorbate does not react chemically with the adsorbent, the adsorbate molecules can be deformed by the action of the most active sites of the adsorbent surface, i.e. the electron layers in the molecule are displaced with respect to the nuclei of its atoms, and the molecule is activated.

If adsorption occurs in solution, ions are adsorbed together with the molecules. The adsorption of ions is called *polar adsorption*. The treatment of water in ion-exchangers is an example of such adsorption.

**Adsorption at the Liquid-Gas Interface.** The adsorption phenomena in liquids are associated with surface tension. The surface tension in a liquid characterizes the state of its surface and is expressed in terms of the work needed to overcome the attraction forces arising between the particles in the surface layer when the molecule appears at the surface. When a substance dissolves in a liquid, the surface tension usually changes. Inorganic salts dissolve in water to slightly raise the surface tension. But the increase is insignificant and can therefore be disregarded.

Organic substances, for example, fatty acids, alcohols, ketones, soaps, proteins, significantly lower the surface tension of water.

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\* Chemisorption is also called *activated adsorption*. Valent bonds are involved in the process, which is also characterized by a high heat effect.

Substances that strongly lower surface tension are known as *surface active substances*, or simply *surfactants*.

Surface active substances are adsorbed by the surface layer, i.e. their concentration there is higher than in the rest of the solution, and they lower the surface tension to an even greater extent.

But the concentration of substances increasing the tension in the surface layer is lower than in the bulk of the solution (*negative adsorption*).

The quantitative characteristics of adsorption are described by the Gibbs adsorption equation derived by thermodynamic calculations:

$$\Gamma = -\frac{c}{RT} \left( \frac{\partial \sigma}{\partial c} \right)_S$$

where  $c$  is the concentration of the solute in the solution;  $\Gamma$  is its excess in the surface layer, mole/sq.cm;  $\left( \frac{\partial \sigma}{\partial c} \right)_S$  is the change in the surface tension of the solution with concentration (the index  $S$  indicates the condition of invariability of surface tension);  $R$  is the gas constant, equal to  $8.314 \times 10^7$  ergs/deg  $\times$  mole;  $T$  is the absolute temperature, K; and  $\sigma$  is the surface tension, ergs/sq.cm.

If surface tension  $\sigma$  decreases with increasing concentration of the solute, i.e. the derivative  $\left( \frac{\partial \sigma}{\partial c} \right)_S$  is negative, then  $\Gamma$  (surface excess) is positive; hence the solute concentration in the surface layer is greater than in the bulk of the solution. If the solute increases surface tension, i.e. the derivative  $\left( \frac{\partial \sigma}{\partial c} \right)_S$  is positive, then  $\Gamma$  is negative. In this case, the solute concentration in the surface layer is lower than in the bulk of the solution (negative adsorption).

The value  $\left( \frac{\partial \sigma}{\partial c} \right)_S$  is assumed to be a measure of the ability of a substance to lower the free energy and is called *surface activity*. The construction of an adsorption curve according to the change in surface tension with the changing concentration of a surface active substance is shown in Fig. 6.15. The curve  $\sigma$ - $c$  is constructed on the basis of experimental data. Next, the value  $\left( \frac{\partial \sigma}{\partial c} \right)_S$  is determined for the points corresponding to the concentrations  $c_1, c_2, c_3$ , etc., by the slope of the tangent to the axis of abscissas;  $\left( \frac{\partial \sigma}{\partial c} = \tan \varphi \right)$ . Multiplying the values obtained for  $\tan \varphi$  by  $c_1/RT, c_2/RT, c_3/RT, \dots$  we find the adsorptions  $\Gamma_1, \Gamma_2, \Gamma_3, \dots$ , from which the Gibbs adsorption isotherm is constructed.

**Adsorption at the Liquid-Liquid Interface.** When two immiscible or only partly miscible liquids form an interface, forces arise that tend to contract the interface to as small an area as possible. These forces are characterized by surface tension at the interface of the two

liquids. If it is necessary to enlarge the interface, work has to be performed.

Adsorption in such systems is also accompanied by a reduction in surface tension. It should be noted that the molecules in the surface layer can in such cases undergo a certain orientation and this has a significant effect on the surface properties of liquids.

**Adsorption on Solid Surfaces.** *Gas Adsorption.* Solid substances can always take up molecules, atoms or ions onto their surfaces from the surrounding medium. For a given adsorbent and a gas or dissolved substance, the amount of adsorbed matter increases with the enlargement of the adsorbing surface. Substances having porous, spongelike structures, or finely divided substances (highly disperse systems, colloids) are characterized by highly developed adsorbing surfaces.

Carbon (charcoal or bone black) stands first in the list of adsorbents. Charcoals are highly porous; their internal surface is as large as 200-500 sq.m per gram. Other porous materials are also used as adsorbents. These include silica gel, quartz sand, caolin, some aluminosilicates, etc.

The absolute amount of the adsorbed substance is determined by the difference between the original amount of the substance and that remaining after the adsorption equilibrium has been attained in the system.

The equilibrium quantity of the adsorbed substance  $x$  per square centimeter of the adsorbing surface  $S$  is called *specific adsorption*:  $\Gamma_{sp} = \frac{x}{S} \left[ \frac{\text{mole}}{\text{sq. cm}} \right]$ . It is difficult to determine accurately the surface area in porous solids and their specific adsorption is therefore expressed in moles per gram of adsorbent, designated by  $A$ :  $A = x/m$ , where  $m$  is the mass of the adsorbent in grams.

Each adsorbent is characterized by maximum saturation  $\Gamma_{\infty}$  under certain conditions:

$$\Gamma_{\infty} = \frac{\text{Maximum quantity of adsorbed substance}}{\text{Adsorbent surface, sq. cm}}$$

The expressions of specific adsorption are interconnected by the following relationship:  $A = \Gamma S_0$ , where  $S_0$  is the adsorbing surface of 1 g of the adsorbent, in sq. cm.

The quantity of a substance adsorbed in one square centimetre of adsorbent depends on the chemical nature of the adsorbent and the adsorbate, on the state of the adsorbent surface, on the adsorbate concentration and the temperature.

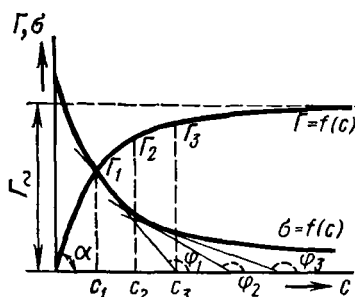


Fig. 6.15. Curves  $\Gamma, \sigma$  vs  $c$

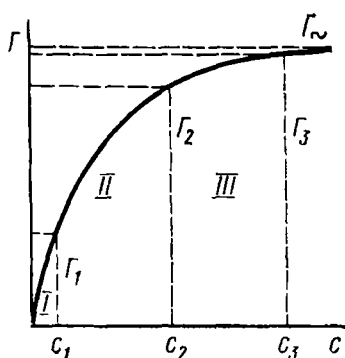


Fig. 6.16. Adsorption isotherm

For a given adsorbent and adsorbate the amount  $\Gamma$  of the adsorbed substance at a given temperature depends only on the equilibrium concentration  $c$  of the adsorbate. Figure 6.16 shows an isotherm of adsorption. The equilibrium concentrations  $c_1$ ,  $c_2$ ,  $c_3$  are plotted against the  $x$ -axis, while the corresponding amounts of the adsorbed substance,  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_3$ , against the  $y$ -axis.

The figure shows that  $\Gamma$  increases with concentration to gradually approach the limiting value  $\Gamma_\infty$ . But this dependence is different for various parts of the curve. At low concentrations (area I), the amount of the adsorbed substance is directly proportional to the concentration of the adsorbate. But in area II adsorption increases slower than in area I, while in area III, for high concentrations of the adsorbate, the curve tends to straighten into a line parallel to the  $x$ -axis, which indicates that the adsorbing surface has been completely saturated.

Various equations are used to analyze the adsorption isotherm, for example, the Freundlich isotherm equation

$$A = Kc^{\frac{1}{\beta}}$$

where  $A$  is the amount of the adsorbed substance in moles per gram of the adsorbent;  $c$  is the equilibrium concentration of the solute in the volume of the phase from which it is adsorbed; and  $K$  and  $\beta$  are constants (found experimentally). Given below are Freundlich constants for activated charcoal:

	$t, ^\circ\text{C}$	$K$	$\beta$
Acetic acid . . . . .	20	0.40	0.97
	50	0.66	0.08
	70	0.75	0.04
Phenol . . . . .	20	0.23	17.18
	70	0.47	2.19

The Freundlich equation does not give all the characteristics of the adsorption isotherm. For intermediate concentrations, when the adsorbent is far from being saturated, it agrees well with experimental data and is therefore widely used. The equation is especially convenient for the transition to logarithmic coordinates, since taking logarithm converts it into the equation for a straight line:

$$\log A = \log K + \frac{1}{\beta} \log c$$

and only two points are needed to construct a straight line.

To construct a straight line the logarithm of concentration is plotted against the  $x$ -axis and the logarithm of the adsorbed substance against the  $y$ -axis.

The starting and final sections of the curve are well described by the Langmuir isotherm arising from the molecular-kinetic theory:

$$A = a \frac{bc}{1 + bc}$$

where  $a$  and  $b$  are constants for the given isotherm;  $A$  is the amount of solute adsorbed in the given quantity of adsorbent;  $c$  is the equilibrium concentration (or gas pressure at the state of equilibrium if the substance to be adsorbed is a gas).

At low concentrations,  $bc$  is considerably less than unity, and can therefore be disregarded in the result. Sometimes the equation has the following form:  $A = abc$ . It expresses the direct proportionality between the amount of the adsorbed substance and its concentration.

With high concentrations,  $bc$  is much greater than unity. In this case, the unity in the denominator can be disregarded and the equation is then transformed into  $A = a$ . This indicates that the amount of substance adsorbed does not change with concentration. Hence the constant  $a$  is the maximum amount of the substance adsorbed by a given adsorbent.

The adsorption isotherm is valid for gaseous and dissolved substances. But compared with gas adsorption, the adsorption from a solution is complicated by the fact that the solvent itself can also be adsorbed. The common form of the isotherm is more likely to change in this case.

**Practical Uses of Adsorption.** Adsorption processes are very important in heterogeneous catalysis with solid catalysts. Adsorption is also used in purification of air in gas masks, in the manufacture of sugar, glucose, in the refining and separation of petroleum products, in the manufacture of pharmaceutical preparations, and in many other branches of industry.

Adsorption is used for the extraction of valuable products admixed with gas or water, for example, for the separation of phenols from water by carbon, or benzene and acetone vapours from air by silica gel. The adsorbed products are then separated by desorption.

Large and small particles are separated from natural water by the soil. The treatment of water in filters and its clarification by coagulation also involves adsorption processes.

Adsorption is important in the biological treatment of effluents. The first step in any sewage treatment process (in irrigation fields, filtration fields, in aeration tanks and methane tanks, biological filters, biological oxidizers) is adsorption, by which the pollutants are separated into activated sludge, active film, or septic sludge.

Destruction of the pollutants (mineralization) is only the second step.

The processes of water desalting or softening in ion-exchangers are based on the polar adsorption principle.

## 6.9. Suspensions

If the size of particles in the disperse phase exceeds 100 m $\mu$ , the system is called a *suspension*.

The separation of the suspended particles by gravity is called *sedimentation* or *precipitation*.

The size of suspended particles can vary from 100 m $\mu$  to 1 mm. If all particles in a suspension are about the same size, the system is called *monodisperse*, and if they significantly vary in size, the system is *polydisperse*.

Sedimentation of particles in a monodisperse system obeys Stokes' law: *at constant temperature, the rate of sedimentation of particles is directly proportional to the square of their diameter*. Stokes' law is expressed by the following formula

$$v = \frac{1}{18} \frac{(\rho_1 - \rho_2)}{\eta} d^2 g$$

where  $v$  is the sedimentation velocity, cm/sec;  $\rho_1$  is the density of the particle, g/cc;  $\rho_2$  is the density of the liquid, g/cc;  $\eta$  is the viscosity coefficient, g/cm  $\times$  sec;  $d$  is the particle diameter, cm; and  $g$  is the gravity constant, cm/sec<sup>2</sup>.

The dependence of the sedimentation velocity on time in a monodisperse system is shown by a straight line inclined to the  $x$ -axis (Fig. 6.17). The line bends at a certain point at which it becomes

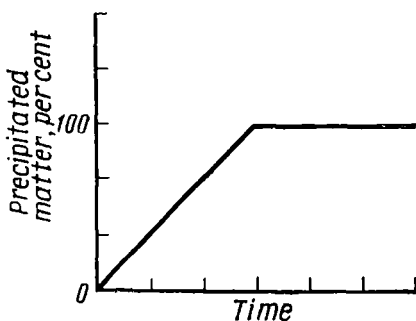


Fig. 6.17. Sedimentation curve of monodisperse system

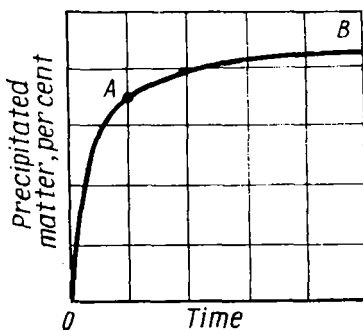


Fig. 6.18. Sedimentation curve of polydisperse system

parallel to the  $x$ -axis. This point corresponds to the complete precipitation of the suspended substance.

In a polydisperse system, the quantity of sedimented substance does not directly depend on time (Fig. 6.18). The curve shows that the main bulk of the suspended substance precipitates during the first minutes (the section  $OA$  of the curve shows sedimentation of coarse particles).

Electrolytes produce the same effect on the velocity of sedimentation of coarse suspensions as they do on the coagulation of colloidal solutions.

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## 6.10. Emulsions

*Emulsions* are systems in which the disperse phase and the dispersion medium are both liquids.

The prerequisite for the formation of an emulsion is the mutual insolubility of the liquids. For example, we can prepare emulsions of oil, benzene, or toluene in water, but it is impossible to prepare an emulsion of alcohol in water.

The mutual insolubility of liquids is due to the different structure of their molecules. One of them contains polar molecules (water), while the other nonpolar or weakly polar molecules (oil). (By oil we understand any organic liquid which is insoluble or only partly soluble in water.)

To stabilize emulsions, special substances are added to the system which are adsorbed at the interface to lower the surface tension. These substances are known as *emulsifying agents* (or simply *emulsifiers*). These are, for example, surface active substances consisting of polar (lyophilic) and nonpolar (lyophobic) parts.

As an emulsifying agent is added to a system, its molecules become oriented at the interface, the polar (hydrophilic) end of the molecules projecting into the water, the nonpolar (hydrophobic) into the oil. The surface tension decreases and the system is stabilized.

Depending on the prevalence in an emulsifying agent of polar (hydrophilic) or nonpolar (hydrophobic) properties, emulsions of two types are distinguished, namely (1) oil-in-water (O/W), and (2) water-in-oil (W/O). The first type of emulsion (O/W) is formed in the presence of an emulsifying agent with predominantly polar molecules, and the latter type (W/O), in the presence of an emulsifier with nonpolar molecules.

Bancroft formulated the following rule: *the liquid which better dissolves the emulsifying agent becomes the dispersion medium*. Therefore, both the type of emulsion and its stability depend on the emulsifying agent, and a change of agent can change the emulsion type, i.e. the emulsion becomes its converse. Emulsions of both types

can be formed simultaneously by mechanical dispersion of liquids, but their stability will be different. The emulsion whose droplets are closely tied to the medium, i.e. are provided with a more lyophilic emulsifying agent persists.

Dilute (less than 1%) and concentrated (over 1%) emulsions are classified by the nature of their aggregation stability. The electrokinetic potential and the associated thickness of the solvate sheath play the main role in the stabilization of dilute emulsions. Droplets bearing like charges are repelled from one another and do not coalesce. With respect to their properties, dilute emulsions resemble lyophobic colloidal systems. The stability of concentrated emulsions depends on the strength of the interface film which is not destroyed on the collision of the droplets. Rebinder and his followers, using their vast experience, have proved that films of substances capable of forming a gel-like structure on the droplet surface produce the best stabilizing action. The film can have the thickness of one molecule (monomolecular) or of several molecules (polymolecular).

The emulsifying agent acts selectively. Therefore, it is selected empirically for each particular system. If the emulsifying agent is properly selected, an emulsion of very high concentration of the disperse phase can be prepared. For example, a 99 per cent emulsion of benzene (O/W) can be prepared in a 1 per cent solution of sodium oleate,  $C_{17}H_{33}COONa$ .

The emulsion type can be determined by the following signs: (1) oil-in-water emulsions readily mix only with water, while water-in-oil emulsions only with oil; (2) O/W emulsions are easily stained with water-soluble dyes, while W/O emulsions with oil-soluble dyes; (3) O/W emulsions have a higher specific conductance than W/O emulsions.

Sometimes the necessity to destroy an emulsion arises. The most effective way to do it is by destroying the emulsifying agent chemically (for example,  $C_{17}H_{33}COONa$  is destroyed by adding acid). A popular method of breaking down an emulsion is by adding surfactant de-emulsifiers which produce an opposing action on the emulsifying agent. These substances displace the emulsifying agent from the droplet surface but do not form chemically stable films themselves. As a result, *demulsification* occurs.

In some industrial processes where two immiscible liquids are required to interact, emulsification solves the problem by increasing the contact surface.

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## 6.11. Foams

A microheterogeneous system consisting of a gaseous disperse phase and a liquid dispersion medium is called *foam*.

Gas bubbles are separated in foams by very thin enveloping films

of liquid which form a kind of a framework, the basis of the foam. The stability of foams depends on the strength of these films. Stable foams are formed in the presence of *foaming* (stabilizing) *agents*\* which are distributed on the surface of the films with orientation of the nonpolar parts of the molecules toward the gas phase and of the polar parts into the liquid. The gaseous phase does not have a great effect on hydrocarbon radicals, nor does it interfere with the formation of structures of stable and elastic films. Foaming agents therefore give structural and mechanical stability to foams.

In order to stabilize a gas bubble, the strength of its walls should be greater than the difference between the capillary pressure\*\*  $p = \frac{2\sigma}{r}$  in the gas bubble and the atmospheric pressure  $p_0$ . Otherwise the bubble will break (where  $\sigma$  is the surface tension;  $r$  is the curvature radius characterizing the curved interface: the radius is positive for a convex meniscus and negative for a concave one). For a flat surface  $r = \infty$ . According to Laplace's equation\*\*\*,  $p = \frac{2\sigma}{r}$ ,  $p = 0$  for a flat surface,  $p > 0$  for a convex and  $p < 0$  for a concave surface. These pressures are combined with the external pressure exerted on the system.

The stability of emulsions and foams is measured by the length of their life  $\tau$  in a  $h$ -cm high column:  $\tau = h/v$ , where  $v$  is the rate delamination of the emulsion or destruction of a foam column of height  $h$  cm (in cm/sec).

The most important industrial use of foams is in the concentration of valuable ores. Foams with thin rigid walls (aerogels) are widely used in the manufacture of heat and sound insulating materials, foam plastics, foam concrete, etc. Foams are also used for the local purification of industrial effluents. The flotation method is used to treat different effluents from insoluble and surface active substances. Even holding effluents (from meat processing and soap manufacturing plants in particular) in flotation units (15-30 minutes on average) ensures their efficient purification (90-98%) both with regard to suspended matter and BOD.

The presence of a flotation-active substance in effluents indicates that froth-flotation methods can be used to treat them without any additional reagents. The presence in effluents of surface active substances causes intense foaming during aeration (in pre-aerators or aeration tanks), which is undesirable for aerobic biochemical processes, since the foam interferes with the contact of the oxygen in the

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\* Emulsifying agents used in O/W systems, such as proteins, soaps, and other substances of organic origin, are good stabilizers.

\*\* The capillary pressure  $p$  is the difference in the molecular pressures between the curved and flat interface.

\*\*\* Laplace's equation is also valid for emulsions.

air with the microflora of the unit. Foam depressing methods are based on the substitution or destruction of the structural adsorption layers which stabilize the foam. Foam breaking agents are substances which displace the stabilizing agent from the surface layer but do not form mechanically stable layers themselves.

To break stable foams, various mechanical, thermal, and other methods are used.

## OXIDATION-REDUCTION PROCESSES

Oxidation reduction reactions are very important in both theoretical and practical aspects. They occur in many processes in chemistry, biology and technology. For example, oxidation-reduction reactions underlie such vital processes as respiration, burning, recovery of metals from ore, metal corrosion, electroplating, etc.

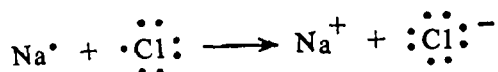
Many methods of treating natural waters and effluents are based on redox reactions. These include the biological treatment of effluents, the catalytic destruction of organic matter by the oxygen of the air, the removal of oxygen from boiler water, the removal of iron and manganese from water, decontamination and dechlorination of water by chemical and physico-chemical methods, etc.

Oxidation-reduction reactions are used in the analysis of natural waters and effluents, for example, the determination of dissolved oxygen (DO), oxygen demanding wastes, ferric and ferrous salts, manganese salts, active chlorine, and other substances contaminating water.

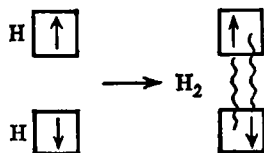
Oxidation-reduction reactions are connected with the electron structure of atoms, the types of valence bonds between them, and also with the ionization energy and electronegativity of elements.

The modern concepts of the valence bond are based on the postulates of classical thermodynamics and quantum mechanics. According to these concepts, the valence bond arises between atoms because of their tendency to assume the energetically more stable state corresponding to the lowest free energy. The chemical bond arises during the interaction of the electrical fields created by the electrons and nuclei of the atoms involved in the formation of molecules. The character of this interaction has been established on the basis of the concept of the atom structure and of the corpuscular-wave properties of the electron.

*The ionic bond* arises between atoms with marked metal and non-metal properties. It is characterized by the electron transfer from the atoms of a metal to nonmetal atoms. As a result, oppositely charged ions are formed between which the electrostatic (Coulomb) attraction is effective:



A *covalent nonpolar bond* arises between the atoms of one element, for example,  $N_2$ ,  $H_2$ ,  $Cl_2$ ,  $O_2$ . This bond is formed by overlapping of the electron clouds of approaching atoms with electrons with opposite spins\*. A shared pair of electrons is thus formed (pairing) according to the following diagram:



The wavy lines in the diagram indicate that each electron moves in a field of force formed by two nuclei of the hydrogen atoms. If the electron density is uniformly distributed with respect to the nuclei of both atoms, a nonpolar bond arises, and hence a nonpolar molecule (e.g.,  $H_2$ ) is formed, while if the electron density is partly displaced toward either of the nuclei, a polar bond is formed, i.e. a polar molecule (e.g.,  $HCl$ ) is formed.

The displacement of the electron density in the formation of polar bonds, and the electron transfer in the formation of ionic bonds is in the direction of more electronegative atoms. The electronegativity of an element is connected with its ionization potential, i.e., the energy of ionization of the atom and its electron affinity.

*The ionization potential of an element is the amount of energy required to remove one electron from the outer level of a neutral atom.* This is normally measured in volts. As an electron is removed from a neutral atom work is performed which is equal to the product of the electron charge and the ionization potential. The work is measured in electron volts.

The ionization potential is a measure of the element's ability to show its reducing properties. These properties are more marked the lower the ionization potential.

The attachment of an electron to a neutral atom or a negatively charged ion is accompanied by the liberation of energy which characterizes the electron affinity. This value is expressed in electron volts per atom, or in kilocalories per gram atom.

The energy of the electron affinity is a measure of the oxidative activity of an element. The higher the electron affinity (i.e. the greater the energy which is liberated during the attachment of an electron to an atom or to a negatively charged ion), the greater the oxidative power of a given element.

The experimental determination of electron affinity is difficult, and the energies for many elements (mostly, for the formation of uninegative ions) have been obtained by indirect methods.

\* Different spin quantum numbers.

The ionization potential and the electron affinity determine the type of bond. All chemical reactions tend to give substances with strong bonds. This saves energy. The weaker the bond, the lower the energy  $E_1$  required to break the bond. The stronger the bond, the greater amount of energy  $E_2$  liberated during its formation. The quantity  $\Delta E = E_2 - E_1$  characterizes the gain in energy.

*The sum of the ionization energy and the electron affinity energy is called electronegativity.*

The electronegativity of the elements increases in each Period of Mendeleev's System according to element's ordinal number. The halogens, the elements located in the main subgroup of the seventh group, have the highest electronegativity.

Linus Pauling has calculated the relative electronegativity of the elements in the Periodic System in such a way that the numerical constant in his equations gives electronegativities expressed within a range of convenient numbers from 0.7 for francium to 4.0 for fluorine. The change in relative electronegativity of the elements in the Periodic System is shown in Fig. 7.1. The direction of the curves shows that relative electronegativity increases from left to right in each period and from the bottom to top in each group.

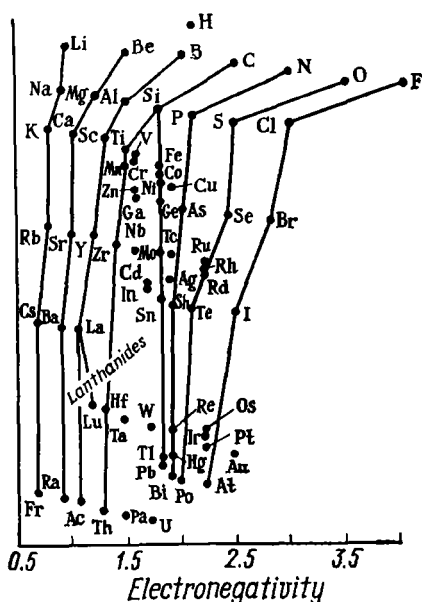


Fig. 7.1. Electronegativities of elements

## 7.1. Oxidation-Reduction Reactions

All chemical processes occurring in nature can be divided into two groups.

The chemical reactions in the first group have the following characteristics:

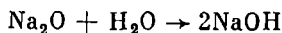
1. The interacting particles do not show electron activity in the course of the reaction.
2. The valency of the elements involved in the reaction is not changed.

These reactions are:

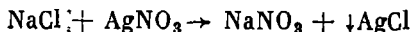
(a) decomposition



(b) combination



(c) exchange



The characteristics of the chemical reactions belonging to the second group are as follows:

1. The chemically reacting particles show electron activity; the electron donor-acceptor function is marked in some elements.

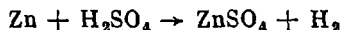
2. The valency of the reacting electron-active elements changes in the course of the reaction.

These are *oxidation-reduction* (redox) *reactions*.

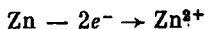
*Oxidation* is the process of giving off electrons by particles of the oxidized element. The algebraic sum of the valency of the element giving off its electrons increases in the oxidation process.

*Reduction* is the process of acceptance of the electrons by particles of the reduced element. The algebraic sum of the valency of the given element decreases in the reduction of the element by the attachment of the "extraneous" electrons.

The oxidizer always accepts electrons in order to reduce itself. Hence, the oxidizer is the *acceptor*. The reducer gives off its electrons and is thus oxidized. The reducer is the *donor*. For example, in the reaction



the zinc atom is the reducer (donor of electrons) while the  $\text{H}^+$  ion is the oxidizer (acceptor):



New types of bond are formed in oxidation-reduction processes. These bonds can be ionic, polar, and nonpolar. Bonds of all types are assumed to be ionic when the valency of the elements is determined. Highly electronegative elements are considered to be negative ions, while positive ions are the elements with low electronegativity. Hence, that ion is negative to which the bonding electron pair is closer. Hydrogen is almost always characterized by positive valency ( $1^+$ ), but oxygen negative ( $2^-$ ). The exceptions to the rule for hydrogen are the hydrides of alkaline and alkaline-earth metals ( $\text{NaH}$ ), where hydrogen is uninegative, and for oxygen, fluorine oxide,  $\text{F}_2\text{O}$ , where oxygen is dipositive. Fluorine is the most electronegative element and therefore it does not show positive valency.

When setting out the equations for oxidation-reduction reactions, the stoichiometric coefficients are first found from the oxidation state of the element before and after the reaction. The oxidation state of an element in a compound is determined by the number of its elec-

trons which are involved in the construction of polar and ionic bonds, while the sign of the oxidation state indicates the direction of displacement of the bonding electron pairs. For example, the oxidation state of the sodium ion in NaCl is +1, and of chlorine, -1.

The oxidation state of an element does not always coincide with its valency, since the latter is determined by the total number of electrons used by the atom to form all types of bonds irrespective of their polarity. The oxidation state is the algebraic sum of all polar bonds. For example, in all chlorine derivatives of methane, the valency of carbon is four, while its oxidation state is different in each new compound:



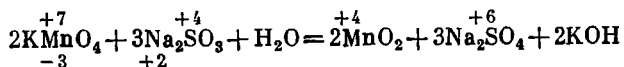
To set out the equation for a redox reaction proceed as follows:

(1) write a skeleton equation of the reaction, showing only the initial reactants and the resulting products;

(2) determine the oxidation state of the elements and superscribe the sign and the oxidation number over each symbol;

(3) deduce the change in the oxidation state of the elements in the given process by subtracting the initial number from the final one and write the sign and the value of the change under the corresponding symbol;

(4) determine the least multiple of the changes in the oxidation number and write the coefficients by oxidizer and the reductant. For example:

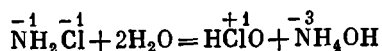


(5) find the coefficients for all elements except hydrogen and oxygen;

(6) check the number of hydrogen atoms and determine the number of water molecules involved in the reaction. Put this number into the either side of the equation;

(7) check the number of oxygen atoms in both sides of the equations and make sure that the equation is balanced.

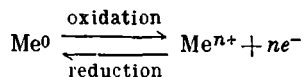
The oxidation state decreases three units in manganese and increases two units in sulphur. Hence, the manganese accepts three electrons (oxidizer) and reduces itself, while the sulphur gives off two electrons (reducer) and is thus oxidized. Consider the hydrolysis of chloramine:



The oxidation state changed as follows: it decreased two units in the nitrogen:  $[-3 - (-1)] = -2$  and increased two units in the chlorine:  $[+1 - (-1)] = +2$ .

## 7.2. Oxidation-Reduction Potential

In the reactions of the second type, an oxidation-reduction potential arises between the reduced and oxidized forms of the substance. For example, if a metal is immersed in a solution of its salt, a certain potential difference is set up between the metal ions in the solution and the metal itself:



These reactions can be arranged in a certain order following the changes in the oxidation-reduction potentials. Table 7.1 shows such an arrangement of the reactions in an electrochemical series. The oxidation-reduction potentials  $E_0$  have been determined with respect to the normal hydrogen electrode\* potential.

The oxidized form of a substance with a higher potential is an oxidizer for the reduced forms with lower potentials, and conversely, the reduced form is a reductant for the oxidized form of the substance having a higher oxidation potential.

For example, the molecular oxygen in an acid medium has potential  $E_0 = 1.23$  V. Hence it can be an oxidizer in all processes characterized by a lower oxidation-reduction potential. The molecular hydrogen is a reductant for all oxidized forms of substances with higher oxidation-reduction potentials.

It follows, therefore, that using the electrochemical series one can decide whether or not an oxidation-reduction process can occur in a given system.

Standard oxidation-reduction potentials determine the possibility or impossibility of the existence of a given substance in a given system. For example, hydrogen sulphide, sulphites, and other substances characterized by lower oxidation-reduction potentials cannot be found in water in the presence of dissolved oxygen.

The oxidation-reduction potentials can be used to determine the changes in the energy of transition of a substance from the reduced into the oxidized state, and vice versa. To that end, one multiplies the standard oxidation-reduction potential by 23.06 to obtain a result expressed in kilocalories per gram equivalent.

For example, as sodium metal is converted into ions (oxidized state), the free energy of sodium decreases  $2.71 \times 23.06 =$

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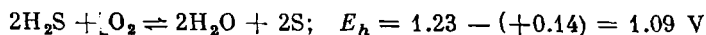
\* The normal hydrogen electrode (or simply the hydrogen electrode) consists of a loose strip of platinum immersed in a 2*N* sulphuric acid solution through which hydrogen is bubbled under a pressure of 1 atm. The difference of potentials between the hydrogen and sulphuric acid is assumed by convention to be zero.

Table 7.1  
Electrochemical Series

Oxidation-reduction process	$E_0$ , V	Oxidation-reduction process	$E_0$ , V
$\text{Li} \rightleftharpoons \text{Li}^+ + e^-$	-3.04	$\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + 4\text{H}^+ + 2e^-$	+0.17
$\text{K} \rightleftharpoons \text{K}^+ + e^-$	-2.92	$\text{CH}_3\text{OH} \rightleftharpoons \text{HCHO} + 2\text{H}^+ + 2e^-$	+0.19
$\text{Na} \rightleftharpoons \text{Na}^+ + e^-$	-2.71	$\text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + 2\text{H}^+ + 2e^-$	+0.19
$\text{Mg} \rightleftharpoons \text{Mg}^{2+} + 2e^-$	-2.38	$\text{Cu} \rightleftharpoons \text{Cu}^{2+} + 2e^-$	+0.34
$\text{Mn} \rightleftharpoons \text{Mn}^{2+} + 2e^-$	-1.18	$\text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2\text{SO}_3 + 2\text{H}^+ + 4e^-$	+0.40
$\text{S}_2\text{O}_4^{2-} + 4\text{OH}^- \rightleftharpoons 2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2e^-$	-1.12	$4\text{OH}^- \rightleftharpoons 2\text{H}_2\text{O} + \text{O}_2 + 4e^-$	+0.40
$\text{SO}_3^{2-} + 2\text{OH}^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}_2\text{O} + 2e^-$	-0.93	$\text{C} \rightleftharpoons \text{C}^{2+} + 2e^-$	+0.51
$\text{H}_2 + 2\text{OH}^- \rightleftharpoons 2\text{H}_2\text{O} + 2e^-$ (pH > 7)	-0.83	$2\text{I}^- \rightleftharpoons \text{I}_2 + 2e^-$	+0.54
$\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2e^-$	-0.76	$\text{MnO}_2 + 4\text{OH}^- \rightleftharpoons \text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2e^-$	+0.60
$\text{Cr} \rightleftharpoons \text{Cr}^{3+} + 3e^-$	-0.74	$\text{H}_2\text{O}_2 \rightleftharpoons \text{O}_2 + 2\text{H}^+ + 2e^-$	+0.68
$\text{Fe}(\text{OH})_2 + \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_3 + e^-$	-0.56	$\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^-$	+0.77
$\text{S}^{2-} \rightleftharpoons \text{S} + 2e^-$ (pH > 7)	-0.48	$\text{Hg} \rightleftharpoons \text{Hg}^{2+} + 2e^-$	+0.79
$\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2e^-$	-0.44	$\text{Ag} \rightleftharpoons \text{Ag}^+ + e^-$	+0.81
$\text{Ni} \rightleftharpoons \text{Ni}^{2+} + 2e^-$	-0.23	$2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4e^-$	+0.82
$2\text{H}_2\text{O} + \text{S}_2\text{O}_8^{2-} \rightleftharpoons 4\text{H}^+ + 2\text{SO}_4^{2-} + 2e^-$	-0.22	$\text{Cl}^- + 2\text{OH}^- \rightleftharpoons \text{ClO}^- + \text{H}_2\text{O} + 2e^-$	+0.89
$\text{HCOOH} \rightleftharpoons \text{CO}_2 + 2\text{H}^+ + 2e^-$	-0.20	$2\text{H}_2\text{O} + \text{NO} \rightleftharpoons \text{NO}_3^- + 4\text{N}^+ + 3e^-$	+0.96
$\text{Sn} \rightleftharpoons \text{Sn}^{2+} + 2e^-$	-0.14	$2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4e^-$ (pH < 7)	+1.23
$\text{Pb} \rightleftharpoons \text{Pb}^{2+} + 2e^-$	-0.13	$\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{MnO}_2 + 4\text{H}^+ + 2e^-$	+1.23
$\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + 2\text{H}^+ + 2e^-$	-0.12	$2\text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2e^-$	+1.36
$\text{C}^{2+} \rightleftharpoons \text{C}^{4+} + 2e^-$	-0.12	$\text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{H}^+ + 2e^-$	+1.49
$\text{Mn}(\text{OH})_2 + 2\text{OH}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O} + 2e^-$ (pH > 7)	-0.05	$4\text{H}_2\text{O} + \text{Mn}^{2+} \rightleftharpoons \text{MnO}_4^- + 8\text{H}^+ + 5e^-$	+1.51
$\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2e^-$ (pH < 7)	0.00	$\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+} + e^-$	+1.51
$\text{NO}_3^- + 2\text{OH}^- \rightleftharpoons \text{NO}_3^- + 2\text{H}_2\text{O} + 2e^-$	+0.01	$1/2\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{H}^+ + e^-$	+1.63
$\text{HCHO} + \text{H}_2\text{O} \rightleftharpoons \text{HCOOH} + 2\text{H}^+ + 2e^-$	+0.056	$\text{MnO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{MnO}_4^- + 4\text{H}^+ + 3e^-$	+1.69
$\text{Mn}(\text{OH})_2 + \text{OH}^- \rightleftharpoons \text{Mn}(\text{OH})_3 + e^-$	+0.10		
$\text{H}_2\text{S} \rightleftharpoons \text{S} + 2\text{H}^+ + 2e^-$ (pH < 7)	+0.14		

62.49 kcal/g-equiv. Hence, in order to reduce a gram equivalent of sodium, the same amount of energy should be spent.

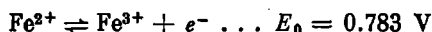
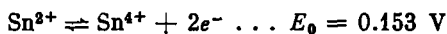
The oxidation-reduction potential of a process is determined by subtracting the smaller value from the greater one. For example, let us determine the oxidation-reduction potential  $E_h$  for the following reaction



Out of all the electrodes and circuits, those electrodes (or circuits composed of them), whose atoms do not participate in the electrode processes but serve only as carriers of the electrons are arranged in a separate group. These are called *oxidation-reduction* electrodes or systems.

What characterizes these systems is that the electrodes are not dissolved in them, nor do the formed substances precipitate, since all reaction products remain in solution.

The oxidation-reduction systems can arise spontaneously when dissolved substances are mixed. Table 7.1 can be used to establish which substances will be oxidized and which reduced in a given system. For example, solutions of iron salts are oxidizers for solutions of tin salts, for equal activities of ions of different valency, since the oxidation-reduction potential of the iron ion is higher than that of the tin ion.



The oxidation-reduction potential  $E_h$ , is, in the generalized form, described by the following expression:

$$E_h = E_0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

where  $E_0$  is the standard potential;  $R$  is the gas constant, 8.314 J/deg;  $F$  is the Faraday number, 96,5000 coulombs;  $n$  is the number of electrons taking part in the process;  $[\text{Ox}]$  is the activity of the oxidized form substance; and  $[\text{Red}]$  is the activity of the reduced form substance.

The oxidation-reduction characteristics of the system in given conditions can be determined from the relationships between the molar or ionic activities of the oxide and protoxide of any substance contained in the medium, since with a mobile physico-chemical equilibrium in a given system, the following ratios can be observed:

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{[\text{Mn}^{4+}]}{[\text{Mn}^{2+}]} = \frac{[\text{S}]}{[\text{S}^{2-}]} = \frac{[\text{X}^{3+}]}{[\text{X}^{2+}]} = \frac{[\text{H}^+]}{[\text{H}]}$$

In practice we often use the ratio between the hydrogen ion and the molecular hydrogen. The oxidation-reduction potential ( $E_h$ ) for

this pair is

$$E_h = \frac{RT}{2F} \ln \frac{[H^+]^2}{[H_2]}$$

$E_0$ , the standard potential for hydrogen, is zero. The exponent 2 indicates that two electrons are involved in the process.

The substitution of all constants and the replacement of natural logarithms with decimal ones ( $\ln = \frac{\log}{0.4343}$ ) gives, for  $t = 25^\circ\text{C}$  ( $T = 273 + 25$ ), the following expression:

$$E_h = 0.029 \log \frac{[H^+]^2}{[H_2]}$$

If the negative logarithm of the hydrogen ion concentration is expressed by pH and of the molecular hydrogen pressure by  $rH_2$  the above equation will be simplified to

$$E_h = 0.029 (rH_2 - 2\text{pH})$$

whence

$$rH_2 = \frac{E_h}{0.029} + 2\text{pH}$$

$E_h$  is the characteristic of free energy of the oxidation-reduction system. It can be determined by measuring the e.m.f. in the circuit consisting of a calomel electrode and a platinum plate (1 sq.cm) immersed in the medium under study, water, or a moist precipitate. Any potentiometer capable of measuring e.m.f. along with the pH of the medium can be used for the purpose. The e.m.f. of a circuit should be expressed in volts with respect to the normal hydrogen electrode. There are no methods for determining  $rH_2^*$ , and this value is calculated using the formula given above.

The value  $E_h$  depends on the molecular hydrogen pressure and on the hydrogen ion concentration. It can be used to characterize the oxidation-reduction conditions only for constant pH. The value  $rH_2$ , however, depends only on the concentration of the reductant, and  $rH_2$  therefore directly characterizes the oxidation-reduction conditions. For example, methylene blue is reduced to 50 per cent at  $E_h$  in the range  $+0.32$  to  $-0.05\text{V}$  and at various pH of the medium. In all cases  $rH_2 = 17$ .

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\* A 'neutral' point, in the sense of the oxidation-reduction conditions for aqueous solutions, is assumed to be  $rH_2 = 28$ . This value is found from the equation of the dissociation of water vapour into oxygen and hydrogen.

For  $t = 18^\circ\text{C}$ , the molecular product of water is  $K_m = [H_2]^2 [O_2] = 10^{-85}$ . Taking logarithm of this equation and substituting the corresponding quantities give  $2rH_2 + rO_2 = 85$ . If hydrogen and oxygen are equimolecular,  $rH_2 = rO_2$ . The substitution of  $rO_2$  in the formula  $K_m$  gives  $3rH_2 = 85$ , and  $rH_2 = \frac{85}{3} \approx 28$ .

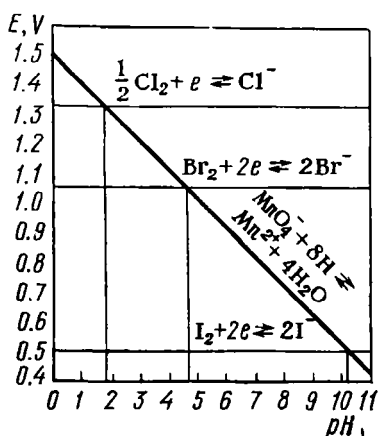


Fig. 7.2. Dependence of redox potential on pH

This is a linear equation of an inclined straight line, where  $m$  is the stoichiometric coefficient for the hydrogen ion;  $n$  is the number of electrons involved in the oxidation-reduction process. Hence, the oxidation-reduction potential strongly depends on the activity of the hydrogen ion if the substances are reduced by hydrogen.

Figure 7.2 shows the change in the oxidation-reduction potential of  $\text{MnO}_4^-$  depending on the pH of the medium. The oxidation-reduction potentials of the systems are shown in the lines parallel to the  $x$ -axis. The system potentials do not depend on the pH and their  $E_0$  are therefore constant. Once the oxidation potential of an oxidizer for various pH and the normal electrode potentials of the mixture components are known, it is possible to perform fractional oxidation of these substances. In our example, the normal oxidation-reduction potentials are as follows:

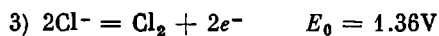
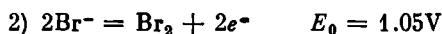
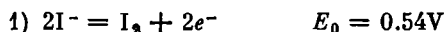


Figure 7.2 shows that in the range of pH from 5 to 10 potassium permanganate will oxidize only iodides, while at pH from 1.8 to 4.7 it will oxidize bromides. Chlorides will be oxidized only at pH below 1.8.

Hence, if we know the normal oxidation-reduction potentials of various systems, it is easy to find the pH of the medium at which a particular oxidation-reduction process can occur, and the relative change in the oxidizing power of a given system can be determined.

The oxidizing power of potassium permanganate is different at various pH. In an acid medium, in the presence of a reductant, it is reduced as follows:  $\text{Mn}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{MnO}_4^- + 8\text{H}^+ + 5e^-$ ;

$$E_h = E_0 + \frac{RT}{nF} \ln \frac{a_{\text{MnO}_4^-} a_{\text{H}^+}^8}{a_{\text{Mn}^{2+}}}$$

At  $t = 25^\circ\text{C}$ ,  $\log a_{\text{H}^+} = -\text{pH}$ , and for  $a_{\text{MnO}_4^-} = a_{\text{Mn}^{2+}}$  we can write this equation in the following form:

$$E_h = E_0 - 0.058 \frac{m}{n} \text{pH}$$

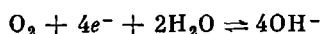
## 7.3. Determination of Oxidation-Reduction Conditions of Fresh Water in Open Bodies

The oxidation-reduction conditions of fresh water in open bodies can be characterized by the oxidation-reduction index  $rH_2$  which can be found from the following equation:

$$rH_2 = \frac{E_h}{0.029} + 2pH$$

If the oxidation-reduction potential  $E_h$  is not determined experimentally, it can be calculated for the given conditions from the Nernst formula, using the pH of water and the coefficient of its saturation with oxygen.

The oxygen dissolved in water is an acceptor of electrons. The process occurs as follows:



The electrode potential  $E_h$  in this reaction is:

$$E_h = E_0 - \frac{RT}{F} \ln \frac{a_{OH^-}}{\sqrt[4]{p_{O_2}}}$$

where  $a_{OH^-}$  is the hydroxyl ion activity;  $p_{O_2}$  is the partial pressure of the oxygen dissolved in water; and  $E_0$  is the normal oxygen electrode potential.

The activity of the hydroxyl ion is connected with the activity of the hydrogen ion by the ionic product of water:  $a_{OH^-} = \frac{K_w}{a_{H^+}}$  or,  $\log a_{OH^-} = pH - pK_w$ . The substitution of all constants and  $\log a_{OH^-}$  into the equation of  $E_h$  for  $t = 25^\circ C$  gives the expression

$$E_h = E_0 - 0.058pH + 0.0145 \log p_{O_2}$$

from which the oxidation-reduction potential of water can be calculated.

The value  $E_0$  for oxygen is the function of pH of the medium and it is therefore determined directly from the graph given in Fig. 7.3 or by the slope of the straight line  $E_0 = f(pH)$  to the x-axis.

Thus, for example,  $E_0$  has its maximum value (1.234 V) in a strongly acid medium (at pH 0); in a neutral medium, at pH 7, 0.828 V, and in a strongly alkaline medium, its value is the lowest, 0.422 V. The electrode potentials ( $E_h$ ) for these systems are as follows:

- 1)  $E_h = 1.234 - 0.058pH + 0.0145 \log p_{O_2}$
- 2)  $E_h = 0.828 - 0.058pH + 0.0145 \log p_{O_2}$
- 3)  $E_h = 0.422 - 0.058pH + 0.0145 \log p_{O_2}$

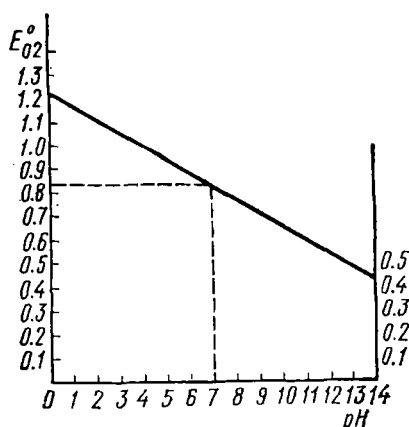


Fig. 7.3. Variation in the normal potential of oxygen depending on pH

Hence, the strong oxidizing power of oxygen shows up only in an acid medium.

**Example 1.** Calculate  $E_h$  and  $rH_2$  of water taken from river N, if its pH is 7.8 and the coefficient of oxygen saturation 90 per cent\*.

*Solution.* 1. Find the concentration of dissolved oxygen at 25°C, since all coefficients in the formula of  $E_h$  are given for this condition.  $pO_2 = 8.28 \times 0.9 = 7.45$  mg/litre.

2. Using the graph in Fig. 7.3, find  $E_0 = 0.779$  V.

3. Substitute the numerical values in the formula of  $E_h$ :

$$E_h = E_0 - 0.058pH + 0.0145 \log pO_2 = 0.779 - 0.058 \times 7.8 + 0.0145 \log 7.45 = 0.339 \text{ V}$$

4. Find  $rH_2 = \frac{E_h}{0.029} + 2pH = \frac{0.339}{0.029} + 2 \times 7.8 = 27.3$ .

Reduction processes prevail here over oxidation processes, which indicates that this part of the water body is polluted with unstable substances (for example, domestic effluents).

**Example 2.** Calculate  $E_h$  and  $rH_2$  of water in river P if its pH is 6.6 and the coefficient of oxygen saturation is, like in the previous example, 90 per cent.

*Solution.* 1. The concentration of the dissolved oxygen is

$$8.28 \times 0.9 = 7.45 \text{ mg/litre}$$

2. Find  $E_0$  in the graph (Fig. 7.3). It is 0.840 V.

3. Substitute the numerical values into the formula of  $E_h$ :

$$E_h = E_0 - 0.058pH + 0.0145 \log pO_2 = 0.840 - 0.058 \times 6.6 + 0.0145 \log 7.45 = 0.468 \text{ V}$$

4. Find  $rH_2 = \frac{0.468}{0.029} + 2 \times 6.6 = 29.2$ .

The high oxidation-reduction index  $rH_2$  shows the presence of strong oxidants in the water (electron acceptors) which is likely to happen when industrial wastes are discharged into open water bodies.

**Example 3.** Determine  $E_h$  and  $rH_2$  in the water of river B if the pH of the water in the sample is 8.2 and the dissolved oxygen saturation coefficient is 121 per cent.

*Solution.* 1. Determine the dissolved oxygen:

$$8.28 \times 1.21 = 10.02 \text{ mg/litre}$$

2. Using the graph (Fig. 7.3) determine  $E_0$ : it is 0.750 V.

3. Substitute the numerical values into the formula of  $E_h$ :

$$E_h = 0.750 - 0.058 \times 8.28 + 0.0145 \log 10.02 = 0.275 \text{ V}$$

\* Oxygen at standard pressure and temperature should be used in the calculation.  $pO_2$  is expressed through an equivalent value (mg/litre  $O_2$ ) with respect to  $E_h$ .

4. Find  $rH_2 = \frac{0.275}{0.029} + 28.2 = 25.88$ .

The oxygen saturation of water in this example is higher than 100 per cent (121 per cent) and despite this fact, reduction processes prevail over oxidation ones. This can be explained by the presence in water of easily decomposing substances necessary for the development of microorganisms which, in the process of their metabolism, decrease the oxidation-reduction potential of the medium.

The above examples show that the concentration of dissolved oxygen in water cannot always be a reliable criterion of the sanitary state of water. The index  $rH_2$  is a more objective characteristic of the processes occurring in a given body of water.

## CHAPTER EIGHT

# CHARACTERISTICS OF NATURAL WATERS

Natural water always contains dissolved and suspended substances of organic and mineral origin. These enter the water with atmospheric precipitation and from soils with which water comes into contact in underground streams or in surface water bodies (rivers, lakes, etc.). Moreover, water is polluted with the metabolites of aquatic plants and animals and the products of their decay.

Plants and animals suspended in water are called *plankton*, while organisms whose habitat is the bottom are called *benthos*. These two aquatic associations have a great effect on the composition of natural waters.

Ground waters contain mostly dissolved substances, while surface waters are rich in suspended matter. For example, the water of the river Amu-Darya contains as much as 5000 mg/litre of suspended matter. The largest amounts of suspended solids are present in open bodies during autumn and spring floods.

There are several classifications of natural waters. They are based on different approaches to the problem.

1. *By their origin* waters are classified as atmospheric (precipitation), subterranean (springs, wells), and surface waters (rivers, lakes, seas).

2. *By the amount and character of impurities* waters are divided into fresh, salt, soft, hard, clear, colourless, opalescing, turbid, coloured, etc.

3. *By their uses* waters are classified as potable, domestic, technical (industrial), cooling, medicinal, etc.

The composition of natural waters usually varies with time. Mineral and organic suspended matter gradually settles by gravity. Part of the organic matter is consumed as food by the living organisms. The chemical and biological processes occurring in natural waters destroy the readily oxidizable organic substances. The formation of hydroxides of iron, manganese and aluminium, and the binding of colloidal admixtures in water by these hydroxides also affect the composition of natural water.

The bulk of the organic matter in natural waters are humins. Proteins, fats, hydrocarbons, organic acids and vitamins also occur in

water, but their presence is insignificant compared with that of organic compounds.

The mineral composition of water is quite varied. Sea water is rich in dissolved substances and is unfit for drinking, or domestic and industrial uses.

Salt content of sea water, g/litre	
Baltic Sea . . . . .	7.5
Black Sea . . . . .	18.0
North Sea . . . . .	32.8
Pacific Ocean . . . . .	33.6
Atlantic Ocean . . . . .	36.0
Mediterranean Sea . . . . .	39.4
Red Sea . . . . .	43.0

The main salt contained in the water of the seas and oceans is sodium chloride (common salt). The approximate salt composition of sea water is as follows:

	%
NaCl . . . . .	83.67
MgCl <sub>2</sub> . . . . .	8.50
MgSO <sub>4</sub> . . . . .	3.60
CaSO <sub>4</sub> . . . . .	4.20
KCl . . . . .	0.03

The water in some lakes is even more salty, up to 5.82 g/litre in Issiq Köl, Soviet Central Asia, and even 360 g/litre in Gusgundag, Transcaucasus.

The composition of so-called *mineral* waters is very interesting. They are absolutely unfit for industrial use but can be valuable medicinal drinks. By their composition they are divided into brackish, alkaline, bitter, containing iron salts, gases, and sulphides. Mineral waters contain from 2.6 to 20.3 g/litre of dissolved substances. Fresh waters contain comparatively small amounts of salts. These are river, lake, ground, artesian and spring waters. They all are drinking waters.

River water usually contains from 0.05 to 1.6 g/litre of salts (more often from 0.1 to 1.2 g/litre). The highest concentration of mineral salts in potable water is in the Thames (Great Britain) and Nile (Africa), which contain 1.6 g/litre of dissolved salts.

The Pechora and Neva (Soviet Union) contain remarkably low quantities of salts, 0.05 g/litre.

Swamp water contains little in the way of mineral salts but is very rich in organic matter. In some cases the concentration is as high as 850 mg/litre.

When we characterize natural waters, the existence of abnormal phenomena should be mentioned. Sea water is known to be salty and unfit for drinking. But fresh water springs frequently occur in coastal areas which are often used for local water supply. The springs are great in number. They are found in karst areas where the coast

and the adjacent sea bottom are of limestone. Atmospheric precipitation, absorbed in karst funnels, wells and crevices, is unloaded through coastal and bottom springs. Subwater springs are found in the Black Sea (USSR). In 1948-1955 they were discovered in the district of Gagra. When the sea is quiet, the movement of water can be easily seen on the surface due to the powerful discharge from a karst spring. Underwater springs are also found in the Crimea, at the Baidar Gates.

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## 8.1. Water Pollutants

The impurities that occur in natural water can be classified into three groups according to their physico-chemical properties.

*The first group.* These are substances which completely dissolve in water. They are present in water as separate molecules or ions. This water cannot be distinguished from absolutely pure water. The presence of impurities can only be detected by chemical analysis or organoleptically (by taste).

Natural water can contain solutions of many gases, e.g.  $O_2$ ,  $N_2$ ,  $CO_2$ ,  $H_2S$  and others, soluble salts of sodium, potassium, calcium, ammonium, magnesium, aluminium, iron, manganese, etc.

Industrial sewage pollutes water with salts of heavy metals (Cu, Pb, Mg) and with various organic substances, such as phenols, formaldehyde, etc.

Dissolved impurities are not retained by sand, paper or any other common filter.

*The second group.* Impurities belonging to this group form colloidal systems with water. The particles of these impurities consist of aggregated molecules. For example, soap particles in water consist of about 50 molecules. Colloidal systems are formed from substances practically insoluble in a given liquid.

The first discovered colloidal systems were of starch, rubber, and glues. Hence the name 'colloid', which originates from the Greek *kolla*, glue. Colloidal particles are so small that they can only be seen with an electron microscope or ultramicroscope. These fine particles are not retained by sand in settling tanks or by paper filters. But they are held by membranes of bovine bladder or collodion.

Substances of mineral origin, such as  $SiO_2$ ,  $Al(OH)_3$ ,  $Fe(OH)_3$ , and organic substances (humins or fulvic acid) can be contained in water in the colloidal state. The latter can colour water from yellow to brown.

*The third group* of pollutants form suspensions in water. These are particles of sand, clay, and organic matter, which are washed off from the soil by rain water, thawing snow and ice, and other runoff.

Pollutants of this kind settle on standing. They are retained by paper and partly by sand filters.

**Biological Contamination of Water.** Natural waters are rich in bacteria, algae, protozoa, worms, and other organisms. The greater the amount of nutrients in water, the faster the biological contaminants develop. The most frequently occurring microorganisms are bacteria which take an active part in the formation of all aquatic populations. They inhabit sludge and other bottom grounds in large quantities and grow into intricate shapes on underwater objects (periphyton). The minutest microorganisms, they are the smallest constituents of plankton (nannoplankton). Bacteria form stable suspensions since their density is close to that of water (their cells contain about 85 per cent of water).

Water plants are also an indispensable part of all aquatic populations due to their high adaptability. Aquatic life includes benthic organisms inhabiting the bottom sludge, plankton living in the water bulk, and organisms developing in the surface layer of water (neuston). Underwater parts of plants, bottom stones and other objects are covered with growths in the form of crusts, pads, and bushes, whose colour varies depending on the composition. Water plants form "underwater meadows" in water bodies rich in soluble salts of calcium.

The density of plankton organisms is close to that of water. Heavy organisms develop the ability to hover in water. They accumulate oils to form mucilage, gas vacuoles (pseudovacuaes), chains, spirals. This increases their volume and reduces their weight. The growth of water weeds is often very intense and the water is said to "bloom".

Water bodies polluted with organic matter of plant and animal origin are a good medium for the development of protozoa. Protozoa feed on bacteria and suspended matter. Some protozoa are carnivorous, for example, rhizopods. They prey on other protozoa, rotifers and small worms.

Water bodies are inhabited by various animals which can be classified as belonging to the large group of worms. They inhabit weed groves, bottom sludge or freely floating plankton formations. Masses of aquatic weeds and sludge are inhabited by larger forms, such as leeches, long and thin oligochetes (scanty-hair worms), flat worms, minute roundworms, and sometimes hair-worms which are 1-1.5 m long. Among microorganisms there are rotifers, both freely floating and living in casings which they build themselves. Microscopic hypotricha also reside here. Their bodies are covered with numerous fine scales topped with little thorns.

Most worms are parasites. They live on the animals or in their internal organs. All aquatic animals and some groups of plants are infested with worms parasitizing on them. Even protozoa and algae

harbour and nourish worms. The parasites are detrimental not only to fishes but, through them, to man as well. But freely living worms are also very useful since fish feed on them. Some representatives of the *Tubificidae* family are involved in the turnover of matter in water bodies by transporting organic substances from deeper layers of the sludge to its surface. Along with other organisms, worms are a good indicator of the living conditions in a water body. They are used by people investigating the sanitary and biological condition of surface waters and for establishing the state of sludge and soil in rivers, which is important for various hydrotechnical constructions.

**Oil Pollution of Water.** The greatest damage to water is inflicted by petroleum and its products. Oil enters water from breakdowns on derricks, wrecks of oil tankers, accidental spillage, cleaning of fuel tanks by merchant and war ships, and also from street cleaning.

According to Thor Heyerdahl (1973), more than 100,000 tons of oil are annually discharged into the Mediterranean Sea. Each square kilometer of the sea surface near southern Italy is covered with 500 litres of masout. The Sargasso Sea is also so heavily polluted with masout that investigators could not take samples of plankton because the cells of their nets got clogged with masout.

According to UN reports, the annual oil influx into the ocean from tankers alone is as much as million tons, while the total amount of oil that enters the ocean is ten times as great.

Oil and its products endanger the aquatic life in the surface layers and also the coastal flora and fauna. Heavy petroleum products precipitate to the bottom or are adsorbed on rock, stone, and sand banks to inhibit the life of the hydrobionts. One drop of petroleum spreads over a great area to isolate the water from contact with atmospheric oxygen, while continuous films inhibit photosynthesis and the formation of oxygen. This inhibits the growth of plankton, which is the main food source of the hydrobionts inhabiting the water body.

All aquatic animals depend, either directly or indirectly, on plankton, which is the basis of the trophic chain, but plankton can develop only in depths of water to which the solar radiation penetrates. In tropics the thickness of this surface layer is 80-100 m, and in the northern regions, 15-20 m (on sunny summer days).

Most organisms inhabiting the surface layers are found near the shoreline, where they obtain the mineral and organic substances required for their vital processes. But the surface of waters in contact with the shore is usually contaminated with oil which interferes with the normal development of many hydrobionts.

## 8.2. Sanitary and Chemical Analysis of Natural Waters

The quality of natural waters is determined by physical and chemical analyses.

**Physical Properties of Water.** These are temperature, odour, taste, turbidity, clarity, colour, density, etc.

The *temperature* of water depends on the season and on the temperature of the ground with which it is in contact. The temperature of water issuing from subterranean springs is little affected by seasonal variations of temperature and is therefore almost constant. The temperature of surface waters varies within a wide range. For example, in the Neva river, it varies, within the year, from 0.1 to 18°C while in the Dnieper river it fluctuates from 1 to 28°C.

The optimum temperature of drinking water is between 11°C and 7°C. Water in this temperature range has a pleasant taste and is refreshing. At high temperatures, water contains little dissolved gases and is therefore unpleasant to taste, nor does it quench thirst. The temperature of water is measured in degrees centigrade and at the moment of taking the sample.

*Odour* and *taste* depend on the temperature, the dissolved gases, and on the chemical composition of impurities (Table 8.1).

The odour and taste of water are due to the presence of, for example, hydrogen sulphide and the products of decomposition of vegetable plants which develop in water bodies. With time, water plants decay under the influence of special bacteria (they become rotten) and liberate substances with unpleasant odours.

A refreshing and pleasant taste is given to water by the dissolved gases (oxygen and carbon dioxide), and also by small amounts of calcium hydrocarbonate.

### Determining of Odour

Odour and smacks are measured on a five-degree scale. The character of the odour is determined first:

(a) odours of natural origin (due to living and decaying aquatic organisms, the shore ground, bottom, environing soils, grounds, well framework, etc.);

(b) odours of an artificial nature (due to accidental industrial pollution, chemical reagents added to water supply systems, etc.).

Table 8.1  
Limit Concentrations  
of Salts Giving Taste to Water

Salt	Concentration, mg/litre	
	indefinite, slight, hardly distinguishable taste	repulsive taste
NaCl	150	500 salty
MgCl <sub>2</sub>	100	400 bitter
MgSO <sub>4</sub>	200	500 bitter
CaSO <sub>4</sub>	70	150 astringent
KCl	350	700 bitter
FeSO <sub>4</sub>	1.5	5.0 chalybeate
MnCl <sub>2</sub>	2.0	4.0 stagnant
FeCl <sub>3</sub>	0.3	0.5 stagnant

Table 8.2

Character of Odour

Sym- bol	Character of odour	Approximate identification
A	Aromatic	Cucumber, flower
S	Stagnant	Silt, miry
P	Putrefactive	Fecal, sewage
W	Woody	Odour of wet chips
E	Earthy	Rotten, freshly ploughed soil
F	Fishy	Cod liver oil, fish
H	Hydrogen sulphide	Rotten eggs
G	Grassy	Hay
I	Indefinite	Natural odour, unclas- sifiable

Table 8.3

Odour Intensity (in degrees)

Degree	Intensity	Description
0	None	Absence of any dis- tinguishable odour
1	Very faint	Odour only detectable by an experienced worker
2	Faint	Odour unnoticeable to an unaware consumer but which can be detected after warning
3	Marked	Odour easily detec- table and giving displeasure
4	Distinct	Odour making water unfit for drinking
5	Very strong	Strong repulsive odour

(c) a person should not carry out routine determinations for long periods of time because of human adaptability to odours and fatigability.

**Determining Taste and Smack.** The taste and smack of water and also their intensities and qualities are determined organoleptically.

All tastes can be roughly classified into four groups: salty, bitter, sweet, and sour. All other taste sensations are smacks. Taste and smack are determined in raw water, except water from open bodies

A wide-neck flask of 150-200 ml capacity is two thirds filled with a water sample, at a temperature of 15-20°C, and covered with a watch glass. The flask is then shaken and rotated, opened, and smelt. The odours of the first group are classified in Table 8.2. Second group odours are named according to the chemical agent which gives the prevailing odour, e.g. phenolic, chlorophenolic, camphoraceous, benzine, chlorine, etc.

The odour of chlorinated water is assessed 30 minutes after chlorination.

The odour is determined (a) at 15-20°C, and (b) after heating to 60°C. The scale of water odours is given in Table 8.3.

The water is heated in the same flask covered with a watch glass.

The following rules should be observed:

(a) the air in the room where the odour of the water is to be determined should have no extraneous odours;

(b) the investigator's hands, face, clothes, etc., should emit no odour;

and springs which are not reliable from the sanitary standpoint. Water from these sources should be boiled, cooled to room temperature, and only then its taste determined. A special note should be put in the test record: "taste, or smack, of *boiled* water". The taste of chlorinated water should be determined 30 minutes after chlorination.

The determination is carried out on a 15-ml water sample which is taken into the mouth, held there for a few seconds and spit out. (Swallowing is not recommended.) The qualitative characteristics of smacks are: chlorine, fishy, metal, etc. The intensity of taste and smack is determined by a five-degree scale similar to that used for the determination of odour.

**Clarity and Turbidity of Water.** Natural waters are often turbid due to the presence in them of suspended particles of sand, clay, silt, or organic matter.

The sources of turbidity of river and lake waters can be soils and rocks which are washed out by the river water from its bed and banks, and also surface particles brought into the water by runoff from meadows, forests, fields, and towns.

An accurate gravimetric determination of suspended matter in water is a time-consuming procedure; indirect methods, namely, the determination of clarity and turbidity, are therefore used.

The determination of clarity is made by: (a) crosses or (b) printed characters. The first method is used for routine control of the work of water treatment plants and for the determination of the quality of tap water, while the second method is used in all other cases.

Figure 8.1 shows the apparatus for determining water clarity. It consists of a 350-cm high cylinder, graduated in 1 cm, on the bottom of which is placed a white disc with a black cross drawn with 1 mm thick black lines and four black spots of 1 mm in diameter between the lines. The bottom of the cylinder is illuminated with a strong electrical light. The greatest height of water in the column, in cm on the cylinder scale, through which the cross and the spots can be distinctly seen, determines the clarity of the water by this method.

Using the other method, the clarity of water is determined in a graduated cylinder held at a distance of 4 cm over standard characters. The maximum height of the water column through which the characters can be read measures clarity.

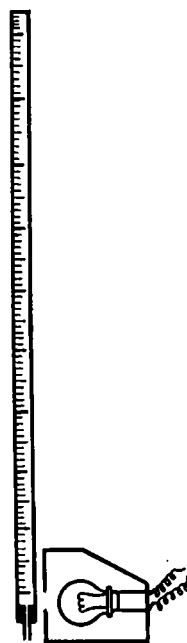


Fig. 8.1. Apparatus for determining solution clarity

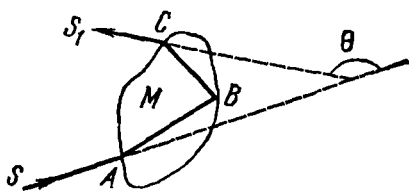


Fig. 8.2. Scattering of light by suspended particles

If a sample of water contains less than 3 mg/litre of suspended matter, the determination becomes difficult because long columns are required. In such cases the characteristic which is the converse of clarity, namely *turbidity*, is determined. A turbidimeter is used for the purpose, turbidity being expressed in mg/

litre. The operating principle of the apparatus is the comparison of the turbidity of a sample water with a standard. The particles of the disperse phase scatter light, and if these particles are larger than the wavelength, the light is scattered due to refraction and complete internal reflection by particles. The scattering of light is shown in Fig. 8.2. The arrow *S* indicates the direction of a light beam which is refracted at point *A* where it meets the particle *M*, then fully reflected at point *B*, and refracted again at *C*. As a result, the path of the beam has deviated by an angle  $\theta$ . Light beams scattered by the particle propagate in all directions to meet the neighbouring particles and to undergo new scattering.

The scattering of light by particles of various size has been studied by Blumer and G. Pokrovsky, who established that *particles of equal size and shape scatter light of equal intensity*.

If two turbid media containing particles of equal size and shape, and having about the same concentration of these particles are taken, the intensity of scattered light will be directly proportional to the concentration.

This principle underlies the design of *nephelometers* which compare the turbidities of two liquids and determine the ratio of concentrations of two suspensions.

One solution of known concentration is used as a standard. By comparing the two liquids, the concentration of the turbid solution in question is determined. Nephelometers are very convenient for the determination of small amounts of substances which are present in cases of slight turbidity.

Particles smaller than light wavelength also scatter light but the cause is different. Reflection and refraction are absent here in the common sense of these words, and what actually takes place is the diffraction of light which comes into contact with colloidal particles. Such scattering of light is called the *Tyndall effect*.

**Colour of Water.** Pure water in a small volume is colourless. Through a thick layer, water has a bluish hue. Other tints indicate the presence of various dissolved substances and impurities.

In order to correctly assess the colour of water, it is necessary first to identify the source of the colour.

The causes which can account for water colour are colloidal compounds of iron, humins, suspended matter, coloured wastes and the intense growth of water plants.

When water "blooms" in open bodies, it becomes light green; when overgrown with blue-greens (protococcous microorganisms) water becomes emerald green.

The colour of natural waters in open bodies is usually due to the presence of humins and fulvic acids\* which colour water various shades, from yellow to dark brown. The colour of water is determined colorimetrically by comparing the colour of water samples with standard colours.

The colour is expressed in degrees of the platinum-cobalt scale (the colour of a solution containing 2.49 g of  $K_2PtCl_6$  and 2.08 g of  $CoCl_2$  in one litre of water is assumed to be 1000 conventional degrees, or of the cobalt-bichromate scale (the colour of a solution containing 0.175 g of  $K_2Cr_2O_7$  and 4 g of  $CoSO_4$  in one litre of water is also assumed to be 1000 conventional degrees, according to the Soviet State Standard GOCT 3351-74).

**Chemical Properties of Water.** The chemical properties of water are very important for a practical assessment of its quality:

- (a) fitness for domestic or industrial use;
- (b) the absence or presence of substances causing corrosion of metals and concrete, or substances which produce foam or scales.

Comparing the results of the chemical analysis of natural water with the requirements for pure water help the investigator to select the best method to treat the natural water.

A complete sanitary-chemical analysis of water comprises the following measurements: (1)\* suspended solids, mg/litre; (2)\* dry residue, mg/litre; (3)\* residue on ignition, mg/litre; (4)\* electrical conductivity,  $\text{Ohm}^{-1} \times \text{cm}^{-1}$ ; (5)\* total oxygen demand, mg  $O_2$ /litre; (6)\* dissolved oxygen, mg/litre; (7)\* biochemical oxygen demand, mg/litre,  $O_2$ ; (8)\* free chlorine, mg/litre; (9)\* chlorine demand, mg/litre; (10)\* active reaction of medium, pH; (11)\* acidity, mg-equiv/litre; (12)\* alkalinity, mg-equiv/litre; (13)\* ions  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Al^{3+}$ ,  $Na^+$ ,  $K^+$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $F^-$ ,  $I^-$ , mg/litre; (14)\* nitrogen-containing compounds: nitrogen of ammonium salts ( $NH_4^+$ ), nitrites, nitrates, mg/litre; (15)\* hardness, mg-equiv/litre; (16)\* carbon dioxide, mg/litre; (a) total, (b)\* free  $CO_2$ , (c)\* hydrocarbonate,  $HCO_3^-$ , (d) carbonate, (e) equilibrium acid, (f)\* aggressive; (17) silica,  $SiO_2$ , mg/litre; (18) surface active substances; (19) hydrogen sulphide,  $H_2S$ ; (20) heavy metal ions,  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Sn^{2+}$ .

\* Fulvic acids are mixtures of various substances; they are the component part of humus which passes into alkaline extract; unlike humins, they remain in solution after acidification. The acids make up about 20% of the soluble part of humus.

A complete sanitary-chemical analysis gives detailed characteristics of water, but it is often possible to limit the analysis to the measurements marked with an asterisk.

Taking the sample is an important step in the analysis of water. The vessel in which the sample is taken should be washed thoroughly, rinsed with distilled water, and then with water from the source in question. The vessel containing the sample should be tightly closed with a ground glass stopper or with a new cork plug.

Rubber plugs should be avoided since water can extract some mineral and organic substances from rubber. When taking samples of tap water (or water from a well), the first container-full should be discarded.

When sampling water from open bodies, the vessel should be immersed into the water so that the sludge on the bottom will not be disturbed; extraneous objects floating on the surface should not be taken either.

Five litres of water is required for a complete sanitary-chemical analysis and for a sanitary analysis, 2 litres.

**Suspended solids.** By suspended solids we mean particles over  $1 \times 10^{-4}$  mm in size which are retained on a paper filter. These may be particles of clay, sand, various silicates, etc. Suspended pollutants are found in surface waters of open bodies. The amount of suspended solids depend on the water protection in a given area and on the season. As a rule, large amounts of suspended solids get into water with thawing snow and rainfalls. Subterranean waters contain lesser amounts of suspended solids because water is separated from them as it passes through the ground.

If the concentration of solids in water is less than 100 mg/litre, they are determined photometrically (nephelometrically) or by filtration through membrane filters. If the concentration is higher than 100 mg/litre, paper filters are used. The photometric method is based on the comparison of the sample with a standard solution in which the concentration of the suspended solids is known. Standard suspensions are prepared from material with which the water in question was in contact. Washed clay is used to prepare a turbidity scale. The particle size of such clays is less than 0.05 mm/sec. As water is examined at water-supply plants, the sludge from the settling tanks and clarification units is used for preparing turbidity standards.

A standard suspension is used to construct a calibration curve which shows the change in absorption depending on the concentration of the suspended solids in solution. The absorption coefficients of the water in question are then determined and the concentration of suspended solids in the sample found from the calibration curve.

The procedure for the determination of suspended solids on membrane filters is the same as with paper filters, but a special apparatus shown in Fig. 8.3 is required to provide a vacuum for suction.

The **dry residue\*** characterizes the concentration of salts and the amount of colloidal substances in water.

The **residue after ignition** refers to nonvolatile impurities contained in water. As a rule, subterranean waters are richer in mineral substances than surface waters, since water dissolves them as it passes through salted soils.

**Electrical conductivity.** Chemically pure water does not conduct electricity. Its specific conductance at  $18^{\circ}\text{C}$   $\kappa = 4.3 \times 10^{-8} \text{ Ohm}^{-1} \times \text{cm}^{-1}$ . Any rise in the electrical conductivity of water indicates pollution with electrolytes.

Oxygen-demanding substances, both inorganic and organic, contained in water and reacting with oxidizers characterize the **total oxygen demand** of water. It is expressed in milligrams of oxygen required to oxidize impurities contained in 1 litre of water.

We distinguish total and partial oxygen demands. The former is sometimes called the chemical oxygen demand (COD) and it is determined on the apparatus shown in Fig. 8.4.

COD is determined by the

\* The dry residue is determined by evaporation of filtrate (according to the Soviet State Standard GOST 18164-72, covering tap water). The Committee for Technical Terminology of the Academy of Sciences of the USSR recommends that this determination should not be named the determination of *dense residue*, since the latter characterizes all water pollutants, suspended solids included. (Terminology of Water Treatment for Boilers, 1956.)

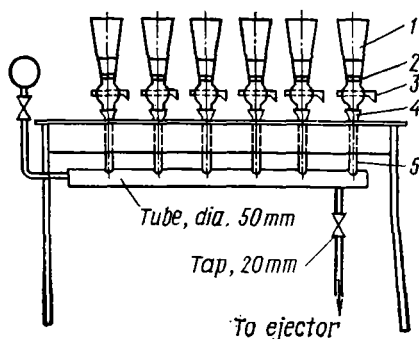


Fig. 8.3. Apparatus for determining suspended particles on membrane filters:

1—funnel (nickel-plated bronze); 2—ceramic porous filter aid; 3—metallic tap; 4—metallic funnel with a rubber stopper; 5—metallic tube

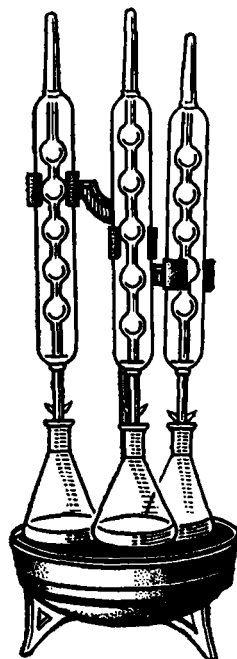


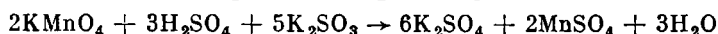
Fig. 8.4. Apparatus for determining chemical oxygen demand

iodate method, which accounts for all the organic substances contained in water. During their oxidation all carbon is burned to  $\text{CO}_2$ , nitrogen is converted into nitric acid, sulphur into sulphuric, and phosphorus into phosphoric acid. For example, the oxidation of acetic acid with potassium iodate in an acid medium can be expressed as:



Partial oxygen demand is determined by the reaction with potassium permanganate  $\text{KMnO}_4$ . Only comparatively easily oxidizable substances are involved in this reaction, but the method is much simpler than the iodate method, and is therefore more popular with analysts.

The oxidation with potassium permanganate is as follows:



The difference in the results of testing a water sample for total and partial oxygen demands indicates the presence of stable organic admixtures in the water.

The oxygen demands of naturally occurring waters depend on humins, hydrogen sulphide, sulphites, ferrous iron, etc.

Artesian waters are characterized by the smallest oxygen demand, about 2 mg of  $\text{O}_2$  per litre. The oxygen demands of ground waters depend on the depth of the source. The deeper the water, the lower the oxygen demand.

Nonpolluted ground waters require about 4 mg/litre of  $\text{O}_2$ , lake waters from 5 to 8 mg/litre of  $\text{O}_2$ , and swamp water up to 400 mg/litre of  $\text{O}_2$ . The oxygen demand of river water varies within wide limits, viz., from 1 to 60 mg/litre of  $\text{O}_2$ .

High oxygen demand of water indicates that the source is polluted and requires cleaning.

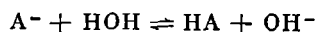
If the oxygen demand of water from a given source increases abruptly, this indicates that it is polluted with domestic sewage. Oxygen demand is clearly an important characteristic of water.

**Chlorine demand**, or the **chlorine absorbing power** of water, is determined by the amount of chlorine, in mg/litre, consumed during a 30-minute contact of chlorine with a given sample of water, and the amount spent to oxidize the impurities contained in the water e.g. humins, products of decomposition of cellular tissues, protein compounds, ferrous salts, nitrites, sulphides, etc.

The chlorine demand of clean waters is not high, from 2.0 to 2.5 mg/litre. A sharp increase in chlorine demand indicates, as was the case with oxygen, the deterioration of the quality of a given water.

Sometimes, in order to describe chlorine demand, a conventional fraction is used in which the numerator is unity, while the denominator describes the dose of chlorine required to ensure the minimum allowed concentration after a 30-minute contact of chlorine with water, equal to 0.5 mg/litre of residual active chlorine.

**Total alkalinity of water.** This is characterized by the presence of all hydroxyl ions capable of combining with the hydrogen ion. Alkalinity in natural water is due to the hydrolysis of salts formed by weak acids and strong bases



When a hydrogen ion is introduced into water, the equilibrium is shifted to the right, and the salt is completely hydrolyzed. The number of milligram-equivalents of acid used to neutralize the hydroxyl ion contained in one litre of water is called *total alkalinity*.

The alkalinity of natural waters depends largely upon the presence of carbonates and hydrocarbonates, while coloured waters can also contain humates (salts of complex organic acids, humic and fulvic acids, entering the water from soil or sludge).

**Determination of the "Humate" Alkalinity.** Organic acids are weak electrolytes and can therefore be displaced from salts with excess mineral acid. This property is the basis of the method used to determine "humate" alkalinity.

A sample of water is first tested for total alkalinity with methyl orange. Next, 1 ml of 0.1*N* hydrochloric acid is added, the sample is boiled for 2-3 minutes and cooled in a jet of water. The solution is titrated with 0.1*N* NaOH solution in the presence of two indicators. The first indicator, methyl orange, is used to indicate the end point of neutralization of the remaining mineral acid (the solution colours yellow at pH 4.4). Then, weak organic acids are titrated with phenolphthalein until the solution colours pink (pH 8).

The number of mg-equivalents of alkali used in the titration of the sample with phenolphthalein and recalculated for one litre is equivalent to the "humate" alkalinity of natural water.

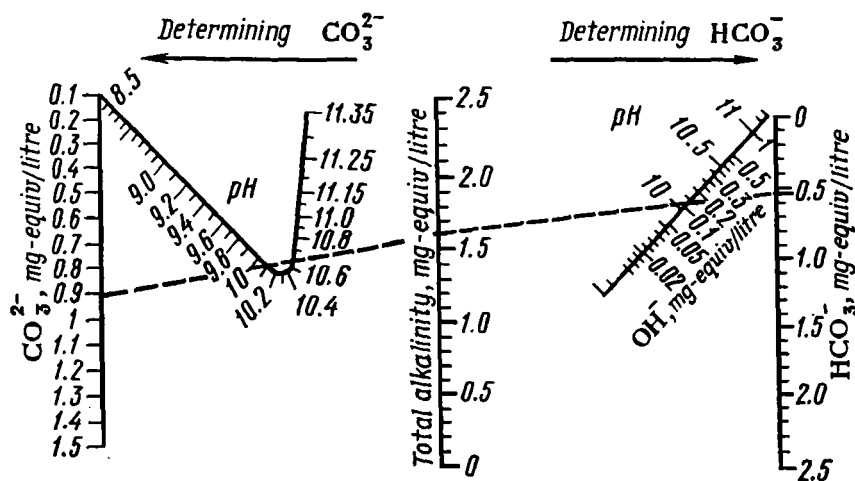


Fig. 8.5. Nomogram for determining three forms of alkalinity ( $HCO_3^-$ ,  $OH^-$ ,  $CO_3^{2-}$ )

Table 8.4  
Correction Coefficients  $\beta$ ,  $\gamma$ , and  $\delta$   
Coefficient  $\beta$

pH	Dry residue, mg/litre					
	50	100	200	300	400	500
8	1.00	1.00	1.00	1.00	1.00	1.00
9	0.99	0.99	0.98	0.97	0.97	0.96
10	0.98	0.95	0.90	0.87	0.85	0.83
11	0.96	0.91	0.84	0.80	0.76	0.73

Coefficient $\gamma$						
8	1.04	1.11	1.25	1.24	1.33	1.39
9	1.04	1.09	1.18	1.24	1.30	1.34
10	1.02	1.05	1.09	1.12	1.14	1.16
11	1.00	1.00	1.01	1.02	1.02	1.02

Coefficient $\delta$ is the same for all pH:						
	1.03	1.06	1.10	1.13	1.16	1.19

equiv/litre;  $[\text{HCO}_3^-] = 0.5$  mg-equiv/litre;  $[\text{CO}_3^{2-}] = 0.9$  mg-equiv/litre. (One of the values is found by subtractions.)

The results obtained from the nomograms are valid only for concentrations of salts not higher than 20 mg/litre. Corrections should be introduced for higher concentrations, i.e. the result should be multiplied by the corresponding coefficients:  $\beta$ —for hydrocarbonate alkalinity,  $\gamma$ —for carbonate and  $\delta$ —for hydrate alkalinity (Table 8.4).

**Hardness of Water.** The total hardness of water is the concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions expressed in mg-equiv/litre. Total hardness is determined complexometrically by titration with Trilon B. The method utilizes the property of Trilon B of making stable, low dissociated complexes with ions of calcium and magnesium.

**The Active Reaction of the Medium.** The pH of most natural waters is close to neutral (6.8-7.3). The constancy of pH in natural waters is maintained by the presence in it of buffer mixtures. If the pH of a given sample of water is not neutral, it indicates that the water is polluted with products of the degradation of organic compounds, chemical effluents from chemical and other plants.

The alkalinity of water is due to the presence of hydrocarbonates of calcium and magnesium, while the acidity of water depends on the hydrolysis of salts formed by weak bases and strong acids contained in water.

**Determination of the Hydrate, Carbonate and Hydrocarbonate Alkalinity by Nomograms.** Forms of alkalinity are determined in practice from nomograms, based on the total alkalinity and the pH of a given sample of water.

For example, let us determine the concentration of free and hydrocarbonate alkalinity in a sample of water if its pH is 10 and the total alkalinity is 1.6 mg-equiv/litre. To that end, draw a straight line to connect the points on the curves corresponding to the given values (Fig. 8.5). The result will show the free and hydrocarbonate alkalinity:  $[\text{OH}^-] = 0.2$  mg-

**Nitrogen Compounds** (ammonium salts, nitrites and nitrates) appear in water mainly through the decomposition of proteinous compounds entering a water body with domestic and industrial sewage. Ammonium nitrogen of mineral origin, formed by the reduction of inorganic nitrogen compounds, is rare in water. If ammonia is formed in water due to the decay of proteins, this water cannot be used for drinking.

The presence of nitrogen-containing pollutants in water indicates its pollution with domestic sewage. If the water has been polluted only recently, all nitrogen is as a rule in the form of ammonia. If nitrites are found along with a  $\text{NH}_4^+$  ion, it indicates that some time has passed since the pollution. If all nitrogen is present in the form of nitrates, a long time has passed since the pollution and water has purified itself.

The above processes are connected with the life of microorganisms of two types. The microorganisms of the first type (nitrite bacteria) comparatively quickly oxidize the  $\text{NH}_4^+$  ion into salts of nitrous acid, while the second-type microorganisms (nitrate bacteria) oxidize nitrites in the presence of large amounts of oxygen (usually at the end of the oxidation processes).

**Chlorine Compounds.** Chlorides are readily soluble in water and the chloride ion is therefore present in almost all waters. Magnesium chloride ( $\text{MgCl}_2$ ) and sodium chloride ( $\text{NaCl}$ ) have the highest solubility (545 and 360 g/litre respectively).

The presence of many chlorides in water could be the result of the washing out of salts from the ground, or by the discharge of domestic sewage into the water. If the water is contaminated with sewage, it contains increased amounts of chloride ion and also ammonia and nitrites, its oxygen and chlorine demands are increased, and there are other indications of water pollution.

The sulphate ion  $\text{SO}_4^{2-}$  occurs in natural waters along with the chloride ion. It enters the water through the dissolution of sedimentary (stratified) rock containing gypsum. Sometimes, the  $\text{SO}_4^{2-}$  ion is formed by the oxidation of hydrogen sulphide or native sulphur. Industrial sewage is another source of this ion.

The sulphate ion content of water in rivers and fresh-water lakes does not exceed 100 mg/litre.

The presence of large amounts of sulphates in water is undesirable, since  $\text{Na}_2\text{SO}_4$  interferes with the normal function of the intestine, while  $\text{CaSO}_4$  and  $\text{MgSO}_4$  give sulphate hardness to the water.

Water containing large quantities of chlorides and sulphates is corrosive. Chlorides destroy concrete by extracting calcium (as calcium chloride) from it. The effect of sulphate water on hydrotechnical structures will be discussed later in more detail.

The ions of iron and manganese occur in natural waters as hydro-

carbonates, sulphates, chlorides, and phosphates, while iron occurs also in the humic complex.

A good deal of iron is contained in chalybeate waters, where its content can be as high as 100 mg/litre. Normal natural waters contain iron quantities of no more than a few milligrams per litre.

The presence of iron and manganese salts in water give it an unpleasant taste and make it unfit for drinking or for industrial and domestic use. Iron salts colour water brown. This water cannot be used for laundering since it stains fabric. Moreover, ferrous and manganous salts promote the growth of specific bacteria in water. Their colonies, and also the products of their metabolism, clog pipes, interfering with the flow of liquids through them.

The manufacture of cinema film, paper, silk, and some other products, requires specially pure water. Water must not contain even traces of iron.

**Silicic Acid.** The presence of silicic acid in water does not impair its taste or adversely affect its sanitary properties. Small doses of silicic acid are harmless to man or animal. The acid is sparingly soluble in water and its content in natural water does not exceed 30-40 mg/litre. It enters water through the dissolution of some silicates.

Silicic acid should not be present in boiler water. The acid is distilled with steam, from which it condenses onto cold parts of the equipment to form a dense and strong deposit.

**Dissolved Oxygen.** Water must be tested for the presence of dissolved gases when one wants to determine its corrosive properties toward metal or concrete. Gases should also be determined in boiler water. Oxygen enters water from the air and it can also be formed in water by weeds growing close to the surface. The solubility of oxygen produced by green plants in water is five times greater than that of oxygen from the air, where the proportion of the gas is 21 per cent (the solubility of oxygen in water depends on the partial pressure of oxygen).

The oxygen concentration in water depends on its temperature and the degree of pollution (Table 8.5). The maximum possible oxygen concentration in water (during dissolution of air) is 14.56 mg/litre at 0°C.

The presence in water of reductants, such as ammonia, ferrous iron, nitrates, readily oxidizable substances and others, upsets the equilibrium upon which the solubility of air oxygen depends and reduces its concentration.

The difference between the oxygen content given in the Table 8.5 and its actual concentration in water at a given temperature is known as the *oxygen deficit*.

Data obtained by Winkler are valid only for the saturation of surface layers of fresh water with oxygen\*.

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\* The oxygen concentration in sea water is lower than in fresh water.

Table 8.5

Dissolved Oxygen in Water at Various Temperatures  
(at 760 mm Hg)

Water temperature, °C	Oxygen content		Water temperature, °C	Oxygen content		Water temperature, °C	Oxygen content	
	ml/lit	mg/lit		ml/lit	mg/lit		ml/lit	mg/lit
0	10.19	14.56	11	7.67	10.99	21	6.23	8.90
1	9.91	14.16	12	7.52	10.75	22	6.11	8.73
2	9.64	13.78	13	7.35	10.50	23	6.00	8.58
3	9.39	13.42	14	7.19	10.28	24	5.89	8.42
4	9.14	13.06	15	7.04	10.06	25	5.78	8.28
5	8.91	12.73	16	6.89	9.85	26	5.67	8.11
6	8.68	12.41	17	6.75	9.65	27	5.56	7.95
7	8.47	12.11	18	6.61	9.45	28	5.46	7.81
8	8.20	11.81	19	6.48	9.26	29	5.36	7.67
9	8.06	11.52	20	6.36	9.09	30	5.26	7.52
10	7.69	11.25						

Winkler suggests that the following formula should be used to determine the dissolved oxygen in deeper layers of water and at other atmospheric pressures:

$$c_1 = \frac{c(B - p + h)}{760 - p}$$

where  $B$  is the barometric pressure, in mm Hg;  $c$  is the oxygen content in a saturated surface layer, mg/litre;  $c_1$  is the same for the layer at depth  $h$ ;  $p$  is the partial pressure of water at a given temperature, in mm Hg; and  $h$  is the half-pressure of a water column ( $\frac{h}{2}$ ), in mm Hg. (For example, for a depth of 3 m, the half pressure of a water column is 111 mm Hg.)

The rate of oxygen dissolution in water (at constant temperature) is directly proportional to the oxygen deficit. This holds for water free from surface film. If deeper layers of water are to be saturated with oxygen, the water must be stirred. The oxygen deficit in water over time  $t$  can be calculated from the formula  $D_t = D_0 \times 10^{-k_2 t}$ , where  $D_0$  is the initial oxygen deficit;  $D_t$  is the deficit after time  $t$ ;  $k_2$  is the velocity constant of oxygen dissolution, which depends on the particular gas, temperature, and the conditions of the surface of the liquid,  $\sigma$ , and the stirring conditions.

Sarma (1967) suggests a method for determining dissolved oxygen in rivers with natural water pollution (that is without human involvement). He offers the equation:  $[O_2] = 12.3 - 0.047 \sum t_5$  where  $\sum t_5$  is the sum of mean daily temperatures of the air during the preceding five days.

A sharp decrease in the concentration of oxygen in water compared with its normal content indicates that the water is contaminated with reductants.

Water used for boilers should be free from oxygen, since it causes corrosion of the equipment at high pressures and temperatures.

**Biochemical Oxygen Demand (BOD)** is the quantity of oxygen, in milligrams per litre, used in the oxidation of impurities in water by biochemical processes occurring in it. BOD characterizes the concentration in water of organic substances to which microorganisms can adapt themselves. Oxygen is used up in the processes connected with their metabolism.

**Hydrogen Sulphide**,  $H_2S$ , is present in water due to the microbiological decomposition of proteins, reduction of gypsum rock, or from sulphides (hydrolysis). The maximum hydrogen sulphide content of water does not exceed ten parts of milligram in one litre. Its presence in water is harmful for fish, and the water smells rotten. Hydrogen sulphide sharply decreases the dissolved oxygen content in water.

**Carbon Dioxide**.  $CO_2$  enters water through the decay of organic remnants in water and soil. The maximum content of carbon dioxide in surface water is 20 mg/litre and in non-mineralized subsoil waters up to 40 mg/litre.

**Iodides and Fluorides**. When selecting a source of water for domestic purposes and drinking, water should be tested for iodides and fluorides. A deficit of these salts in drinking water is detrimental to man and causes serious diseases. The daily requirement of iodides is 300  $\mu g$ /litre.

The human body is very sensitive to fluorides in the diet. Their importance is confirmed by the presence of fluorides in bone tissues and tooth enamel. Fluorine deficiency in drinking water (below 0.7 mg/litre) causes tooth caries. At the same time, excess fluorine (over 1.5 mg/litre) causes fluorosis (mottled tooth enamel)\*. The optimum dose is within a narrow range, viz., from 0.7 to 1.5 mg/litre\*\*. If water lacks the necessary amount of fluorides, they are added artificially.

**Heavy Metal Ions (Pb, Cu, Zn, etc.)**. These metal compounds are usually poisonous and get into water with industrial effluents and municipal sewage.

Arsenic and poisonous cyanides enter water with the sewage of tanning, dye-staff producing, cotton printing and metal working plants.

**Synthetic Surface Active Substances (Surfactants)**. These are substances which affect (usually reduce) surface tension. These comprise

\* Fluorosis occurs in localities where artesian waters are used for drinking.

\*\* According to the international standard (adopted in 1963) the fluorine content of drinking water shall be within the range of 1 to 1.5 mg/litre.

also surface active substances obtained artificially (by synthesis). They are contained in the surface layers in greater concentrations than in the inner parts of liquid. Surfactants which form micellar colloids (colloidal electrolytes) are the most important ones. These are open-chain organic compounds containing from 10 to 20 carbon atoms. Their molecules also contain hydrophobic radicals and hydrophilic groups characterized by a certain optimum balance of hydrophilic and hydrophobic properties.

Depending on their properties, synthetic surfactants are classified as *ionogenic* and *nonionogenic*. Ionogenic synthetic surface active substances are salts of fatty, alkylsulphuric, alkylphosphoric acids, alkyl-ammonium bases, which practically completely dissociate into ions. Esters comprising chains of hydrophilic ethoxy groups, type  $C_nH_{2n+1}COO(CH_2CH_2O)_mH$ , (where  $n$  is from 6 to 18,  $m$  can vary from a few units to hundred) are nonionogenic synthetic surfactants. The  $-CH_2O-$  parts of the chain are hydrophilic and  $-CH_2-$  are hydrophobic.

Synthetic surfactants are much used as flotation agents, stabilizers, detergents, etc.

The detergent action is a complicated colloidal-chemical process comprising the reduction of surface energy, dispersion, colloidal protection, and solubilization\*.

Detergents are synthetic surfactants of a special type. In addition to strong surface activity and wetting power, they have a high stabilizing effect on hydrophobic particles of dirt. The washing action is in two stages: wetting the surface, during which dirt particles pass into the liquid, and stabilizing these particles to preclude their sticking together and reprecipitating on the surface.

Synthetic surfactants are widely used for domestic and industrial purposes. When synthetic surfactants get into natural water bodies they form films on the water surface to interfere with normal aeration and inhibit self-purification of water from other pollutants. Large amounts of synthetic surfactants in sewage interfere with the normal operation of sewage treatment plants (primary settling tanks), inhibit the biochemical processes on biological oxidizers and promote foaming. Sanitary regulations therefore stipulate that the allowable concentration of synthetic surfactants in sewage intended for complete biological purification should not exceed 20 mg/litre for ionogenic and 50 mg/litre for nonionogenic surfactants, provided the sewage is first mineralized biologically to 80 and 90 per cent respectively. If the sewage contains both ionogenic and nonionogenic surfactants, their total concentration should not exceed 20 mg/litre. If synthetic surfactants cannot be treated biologically they should not be allowed in the general sewage system.

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\* Pseudodissolution of hydrocarbons (e.g. benzene, heptane, kerosine, mineral oils) in aqueous solutions of synthetic surfactants.

### 8.3. Requirements for Water Quality

Depending on the requirements, water can be classified as follows:

1. Potable water; water for cooking and drinking.
2. Cooling water (cooling of machinery, liquid and gas products in condensers and coolers).
3. Water for boilers.
4. Technical water used at various stages in the manufacture of paper, textiles, leather, etc.
5. Irrigation water, etc.

Depending on the purpose, the physical, chemical and bacteriological properties of water should meet special requirements. These determine the selection of water supply sources, the technology of water processing, and the layout of sewage treatment plants.

**Drinking water.** It should be harmless to man, must have good organoleptic properties, and should be fit for domestic use. The Soviet State Standard (ГОСТ) No. 2874-73 covering the quality of drinking water reads as follows:

#### Requirements for Drinking Water

##### *Bacteriological Characteristics:*

Total number of bacteria in 1 ml of nondiluted water should not exceed . . . . .	100
The number of bacteria of the <i>E. coli</i> type:	
as determined on a dense elective medium with bacteria concentration on membrane filters, in 1 litre of water (coli indicator), should not exceed . . . . .	3
in examination of liquid media accumulating coli titre, should not be less than . . . . .	300

##### *Toxic Chemicals in Water*

(Allowed concentrations of chemicals in water)

Beryllium, mg/litre . . . . .	0.0002
Molybdenum, mg/litre . . . . .	0.5
Arsenic, mg/litre . . . . .	0.05
Nitrates, mg/litre . . . . .	10.0
Polyacrylamide, mg/litre . . . . .	2.0
Lead, mg/litre . . . . .	0.1
Selenium, mg/litre . . . . .	0.001
Strontium, mg/litre . . . . .	2.0
Fluorine, mg/litre . . . . .	0.7
	(depending on climate)
Uranium, naturally occurring and $U^{238}$ , mg/litre . . . . .	1.7
Radium 226, curies*/litre . . . . .	$1.2 \times 10^{-10}$
Strontium 90, curies/litre . . . . .	$4.0 \times 10^{-10}$

\* Curie is the standard unit of radioactivity, describing the quantity of a substance which gives the same number of disintegrations as 1 g of radium, i.e.  $3.7 \times 10^{10}$  disintegrations per second; 1 microcurie =  $10^{-6}$  curie.

*Notes:*

1. If, for local reasons, water is fluorinated, its fluorine content should be within the limits of 70-80 per cent of the specified norm.

2. If silver ( $\text{Ag}^+$ ) is used for the preservation of water, the ion content should not exceed 0.05 mg/litre.

3. If several toxic substances are revealed in water (except fluorides, nitrates, and radioactive substances), the total concentration, expressed in fractions of the maximum allowed concentration of each individual toxic substance, should not exceed 1.

Use the following formula for calculations:

$$\frac{c_1}{C_1} + \frac{c_2}{C_2} + \dots + \frac{c_n}{C_n} \leq 1.$$

where  $c_1, c_2, \dots, c_n$  are the concentrations to be measured mg/litre; and  $C_1, C_2, \dots, C_n$  are specified standard concentrations, mg/litre.

**Organoleptic Characteristics**

These should meet the following requirements:

Odour, at 20°C and with heating to 60°C, degrees . . . . .	2 max
Smack, at 20°C, degrees . . . . .	.2 max
Colour, on platinum-cobalt scale, degrees . . . . .	.20 max
Turbidity, on standard scale, mg/litre . . . . .	1.5 max

*Note:* In special cases it can be 35 degrees

(by agreement with the sanitary and epidemiological service)

pH . . . . . from 6.5 to 8.5

If taste-affecting substances are found in water (sulphates, chlorides) their total concentration, expressed in fractions of the maximum allowed concentration of each individual substance, should not exceed 1.

Dry residue, mg/litre . . . . .	1000.0
Chlorides ( $\text{Cl}^-$ ), mg/litre . . . . .	350.0
Sulphates ( $\text{SO}_4^{2-}$ ), mg/litre . . . . .	500.0
Iron ( $\text{Fe}^{2+}, \text{Fe}^{3+}$ ), mg/litre . . . . .	0.3
Manganese ( $\text{Mn}^{2+}$ ), mg/litre . . . . .	0.1
Copper ( $\text{Cu}^{2+}$ ), mg/litre . . . . .	1.0
Zinc ( $\text{Zn}^{2+}$ ), mg/litre . . . . .	5.0
Residual aluminium ( $\text{Al}^{3+}$ ), mg/litre . . . . .	0.5
Hexametaphosphate ( $\text{PO}_3^-$ ) <sub>6</sub> , mg/litre . . . . .	3.5
Phosphate ( $\text{PO}_4^{3-}$ ), mg/litre . . . . .	3.5
Total hardness, mg-equiv/litre . . . . .	7.0

*Notes:*

1. With the agreement of the local sanitary and epidemiological service, dry residue can be up to 1500 mg/litre and the total hardness 10 mg-equiv/litre.

2. If iron is not removed from subsoil water its content in tap water can (with the agreement of the local sanitary and epidemiological service) be up to 1.0 mg/litre.

FOCT 2874-73 covers all waters used in the processing of foods and drinks.

Water used in the *processing of sugar* should be free of organic substances highly susceptible to decomposition in order to preclude

fermentation in diffusers. The level of salts should be at a minimum since their presence interferes with the boiling and crystallizing of sugar.

Water used for the *manufacture of beer* should be free of calcium sulphate,  $\text{CaSO}_4$ , which inhibits malt fermentation.

Water used in the *manufacture of alcoholic liquors* should be free of chlorides of calcium and magnesium since they inhibit the growth of yeast.

Other branches of the food industry have their own individual requirements for the quality of water.

**Cooling Water.** Untreated natural water is normally used for cooling purposes. The requirements for cooling water are (a) as low a temperature as possible; (b) the lowest possible temporary hardness; (c) least possible amounts of suspended matter, particularly of organic origin; (d) insignificant permanent hardness. It must not corrode the equipment.

Suspended matter is especially undesirable, since it combines with compounds causing temporary hardness, and so form deposits on the walls of heat-exchange apparatus.

If the temperature drop in condensers is insignificant, organic matter contained in water provides the conditions for the growth of microorganisms whose propagation can clog the pipes.

**Water for boilers** should meet the following requirements:

- (a) the lowest possible total hardness;
- (b) the lowest possible permanent hardness;
- (c) the lowest possible silicic acid content;
- (d) the water should be free from substances promoting the formation of stable foams (oils, resinous or organic matter);
- (e) the water should be free from dissolved gases ( $\text{CO}_2$ ,  $\text{O}_2$ ), free acids, and magnesium chloride ( $\text{MgCl}_2$ );
- (f) the minimum allowed quantity of oils in feed water for medium pressure boilers is 2 mg/litre and for high pressure boilers up to 1 mg/litre.
- (g) the oxygen content of water for low-pressure boilers should not exceed 3 mg/litre; oxygen in the water inadmissible for medium- and high-pressure boilers.

The strict requirement on the absence of oils is explained by the fact that they cause foaming of water, while oxygen corrodes the equipment.

**Technical Water.** The requirements for technical water depend on the purpose for which it is to be used. For example, the cinema film, textile, and paper industries require that water should be free from iron, manganese, silicic acid, and only limited quantities of chlorides, organic matter, etc., are allowed.

Water used in the manufacture of man-made fibres should not use more than 2 mg/litre of  $\text{O}_2$  for its oxidation. It must be soft

(0.17 to 0.64 mg-equiv/litre), and its iron content should not exceed 0.03 mg/litre.

Water used in silk manufacturing and dyeing factories should be completely free from iron (not even traces should be evident) and organic matter.

The tannery requires soft water, because the salts responsible for the hardness of water deteriorate tanning agents. Putrefaction bacteria and fungi impair the strength of tanned leather and their presence in water is therefore inadmissible.

Foliage, water weeds, etc., should be absent from water used in the manufacture of starch, since they colour it brown. Iron should also be absent because it colours starch yellow.

**Irrigation Water.** This is used in agriculture and should not contain salts in quantities greater than 1.5 g/litre.

Excess salts in soils are detrimental to crops. Large quantities of  $\text{Na}^+$  ion are especially harmful to plants.

## CHAPTER NINE

# MAIN PROCESSES IN WATER PURIFICATION

The selection of a method for the purification of water depends on the specific requirements for the water. Given below are the main methods which are commonly used for the practical purification of water.

1. Removal of coarse particles by settling, filtering, filtering with preliminary coagulation, or a combination thereof.
2. Coagulation (removal of fine disperse particles).
3. Disinfection of water by removal of pathogenic microbes.
4. Water stabilization by removal of substances causing the corrosion of metal and concrete.
5. Removal of dissolved gas.
6. Removal of odour and taste (deodoration).
7. Softening and desalting.
8. Conversion of temporary hardness into permanent. (Softening with hydrochloric or sulphuric acid.)
9. Desalting water highly laden with salts.
10. Correction of the iron, manganese, silica, and fluorine content.
11. Removal of radioactive substances.

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### 9.1. Removal of Coarse Suspended Particles

Coarse particles suspended in water can be removed by *settling*. This method is used as an independent part of the water purification process, and also after treating it with a coagulating agent.

In order to accelerate settling, water is first passed through a filter packed with sand, keramzit, anthracite, and other filtering agents. The distribution of the suspended matter in the filtering bed varies according to the rate of filtration. If the rate is slow the suspended matter is retained in the upper layers; while at a high rate it is retained in the depth of the filtering bed, because the hydraulic forces prevent the formation of films. When water is passed through a granular filter, the suspended matter is adsorbed physically by noncompensated van der Waals' forces. Experience shows that if a filter is

packed with coarse granules and the filtration is fast, the pollutants penetrate greater depths of the filter. This is due to the smaller specific surface of the coarse granules, producing a weaker attractive force holding the pollutants.

The charge on a suspended particle is important for the clarification process. If the granule surfaces of the filter and the suspended particles bear the same charge, the particles will not be retained well enough on the filter.

Consider the process of filtration through a porous material in a *slow filter*. These filters are used to clarify turbid and slightly coloured waters. The filtration rate through slow filters depends on the turbidity of the water. It is from 0.3 to 0.4 m/h for turbidity up to 25 mg/litre and from 0.2 to 0.3 m/h for turbidity from 25 to 50 mg/litre.

A slow filter (Fig. 9.1) is a tank packed with sand and gravel. The upper layer, about 1-1.2 m high, is actually the *filtering* one, since suspended matter is retained in it. It consists of clean quartz sand, with particles ranging from 0.25 to 0.35 mm. The lower layers consist of coarser sand and gravel.

The depth of the water layer above the sand is about 1 m. As time passes, a film is formed on the surface of the filtering material. This film is formed of various suspended substances retained on the filter. After two or three months, the film is about 20 mm thick. A dense film can retain particles of various size, and even microorganisms contained in water. This film is called *biological*. The dense film decreases the filtration rate and it is therefore removed from time to time with the upper layer of the sand, and fresh sand is added.

The decontaminating action of the filter begins only during the middle period of its use. During the initial period, the large pores fail to retain microorganisms, while after prolonged use, its own microflora develops in the filter and the water, cleaned in the upper layers of the filter, will be contaminated by this microflora as it passes through the lower layers.

The slow filtration method is applicable to waters with colour up to 35°. The clarifying effect is high with turbid water. The filter does not require chemicals, its own water requirements are low, and the design is simple. The slow filtration method can be used for small-capacity water supply systems, e.g. in rural areas.

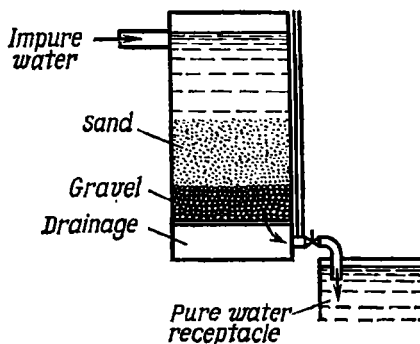
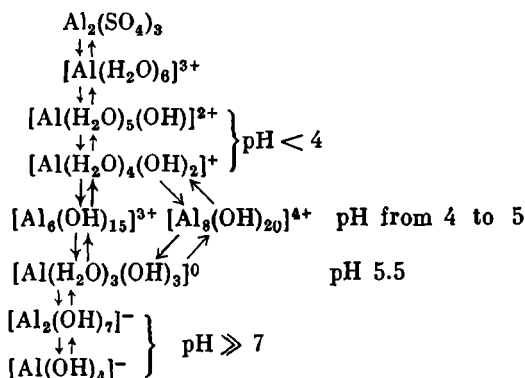


Fig. 9.1. Sand filter

## 9.2. Coagulation

Fine disperse particles are removed from water by coagulation, that is, by *treating the water with a special reagent which enlarges particles to promote their precipitation.*

The coagulation process is used to clarify and decolour water. Natural waters are polluted with humins, clay, silica, etc. Particles of these substances bear a negative charge. They are removed by coagulation with salts of weak bases and strong acids. The coagulants enter into an exchange reaction with the water ions to form complex coordinated compounds. Aluminium sulphate is normally used for the purpose. The hydrolysis of this reagents gives complex ions whose charge depends on the pH of the medium. In the diagram below, F. Winkler arranges the products of hydrolysis of  $\text{Al}_2(\text{SO}_4)_3$  in order of their increasing pH:



Of all hydrolysis products, the most important are the coordination compounds with six or eight atoms. These form, with neutral particles  $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3]^0$ , a reticular positively charged structure promoting coagulation of natural waters.

The salt composition of water has a significant effect on the process of coagulation. Anions of weak acids account for the capacity of the buffer, and promote hydrolysis of the coagulant. Cations can alter the charge on colloidal particles. For example, in hard waters negatively charged colloids can become charged positively because of the adsorption of calcium and magnesium ions. At pH above 7, this charge can be neutralized with  $\text{SO}_4^{2-}$  ions of aluminium sulphate, while the aluminium ion will completely hydrolyze to  $\text{Al}(\text{OH})_3$ . The coagulant dose will be smaller than for coagulation of suspended clay with negatively charged particles. Hence, the  $\text{SO}_4^{2-}$  ion-partner significantly promotes the coagulation process in hard waters. When the coagulant is added to water, the double electrical layer of particles is compressed so that particles approach each other to a distance

where the intermolecular attraction force becomes sufficient to enlarge the particles.

The prerequisite condition for mutual coagulation is the equality of opposite charges of sol particles. If this condition is not fulfilled, coagulation is incomplete whatever the coagulant concentration may be. Thus, mutual coagulation becomes possible only within a narrow range of concentrations (see Chapter 6).

According to GOCT 2919-45, the optimum dose of coagulant for each water sample should be determined in the laboratory. *The optimum dose is the lowest concentration of a coagulant giving the maximum clarifying effect.*

Figure 9.2 shows a curve describing the coagulation of a fine clay suspension with aluminium sulphate. When the coagulant concentration is low, the turbidity of the water does not change (zone I), but as the concentration increases, the turbidity sharply decreases to a certain limit (zone II). At a coagulant concentration of about 20 mg/litre, the charges on the colloidal particles will be mutually neutralized. If the coagulant dose increases to over 100 mg/litre, the colloidal particles become recharged and water turbidity can increase to the initial level (zone III).

When water is tested for coagulation, the following factors should be taken into account: temperature, pH of solution, stirring intensity, salt composition of the water sample.

Beside the determination of the required dose of the coagulant, the laboratory test should also establish (1) the rate of flocculation, (2) the kinetics of precipitation, (3) the kinetics of the process by which the precipitate is compacted. These data are necessary to choose rationally the equipment for coagulation and settling.

A tentative calculation of the optimum dose of a coagulant, depending on turbidity and colour of the water, can be done using the following empirical formulas:

(a) for turbid waters

$$D_c = 3.5 \sqrt{T}$$

(b) for coloured waters

$$D_c = 4 \sqrt{C}$$

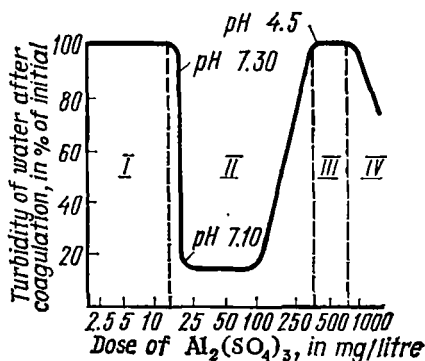
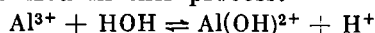


Fig. 9.2. Determining the optimum dose of coagulant

where  $D_c$  is the dose of the coagulant, anhydrous aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3^*$ , in mg/litre;  $T$  is the turbidity of the water, mg/litre;  $C$  is colour, in degrees of the platinum-cobalt scale.

For successful hydrolysis of the coagulant, it is necessary to bind the hydrogen ion formed in this process:



If the coagulant is applied in excessive quantities, the natural alkalinity of the water may be insufficient to bind hydrogen, and lime is therefore added. The required quantity of lime can be calculated by the formula:

$$D_{\text{lime}} = \left( \frac{D_c}{57} - \text{WA} + 1 \right) 28$$

where  $D_{\text{lime}}$  is the dose of lime,  $\text{CaO}$ , in mg/litre;  $D_c$  is the coagulant dose, in mg/litre;  $\text{WA}$  is the alkalinity of the water, in mg-equiv/litre; 1 is the lime excess, in mg-equiv/litre; 28 is the equivalent weight of calcium oxide,  $\text{CaO}$ ; and 57 is the equivalent weight of  $\text{Al}_2(\text{SO}_4)_3$ .

When alkalyzing water, care should be taken not to exceed the required pH, since otherwise the aluminates  $[\text{Al}_2(\text{OH})_7]^-$  can be formed, and aluminium hydroxide will not precipitate.

Alkalyzing is not recommended for the treatment of swamp water rich in humins. The coagulating effect can be increased by acidifying. In this case, weakly dissociating humins lower their charge and the particles coagulate to form unstable low-disperse readily coagulating sols. Excess acidification should be avoided as well, since humins can coagulate spontaneously and the water will become corrosive; hence it will require further alkalyzing.

**Contact Coagulation.** This process is based on the ability of small particles to adsorb on large particles of sand or suspended precipitate through which water is filtered.

An optimum dose of a coagulant is added to the water before filtration and the diffuse layer of the particle is compressed (the system passes to an almost isoelectric state). The particle enlargement process is accelerated by collision with the granular charge of the filter.

During filtration, fine particles come in contact with sand or precipitate grains and van der Waals forces become effective, accounting for the physical adsorption. This is confirmed by the rate of clarification of water within 5-10 seconds (the time characteristic of

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\* The required dose of  $\text{Al}_2(\text{SO}_4)_3$  is calculated by the following formula:  
 $D_{\text{Al}_2(\text{SO}_4)_3} = \frac{29.8a}{b}$ , where  $a$  is the optimum dose of  $\text{Al}_2(\text{SO}_4)_3$ , mg/litre;  $b$  is the  $\text{Al}_2\text{O}_3$  content of the product used, in per cent; 29.8 is the percentage of  $\text{Al}_2\text{O}_3$  in 100 per cent aluminium sulphate. The optimum dose of lime ensuring a good clarifying effect is calculated by the formula  $D_{\text{CaO}} = \frac{100a_1}{b_1}$ , where  $a_1$  is the dose of calcium oxide, mg/litre;  $b_1$  is the  $\text{CaO}$  content of commercial lime, in per cent; 100 is the conversion factor for lime of chemical purity.

physical adsorption) instead of 20-40 minutes of the ordinary coagulation process.

The high speed of clarification depends on the greater probability of collision between fine and coarse particles than between fine particles alone.

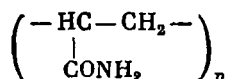
Experiments show that contact coagulation gives more effective clarification and cuts the time needed to purify water of suspended matter.

**Intensifying the Coagulation Process.** The coagulation process can be intensified by adding special agents known as *flocculants*. These are substances forming colloidal disperse systems with water. Flocculants work probably by neutralizing the charge on the colloidal particle of the coagulant and by destroying the protective properties of some colloids (a flocculant can figuratively be called a coagulant of coagulants).

Sometimes flocculants are used to coagulate fine disperse particle contained in natural waters and sewage, without using any coagulants. The flocculant can act like a coagulant only if the suspended matter is in an unstable state of aggregation and its concentration is considerable.

The way a flocculant works is explained by some authors as follows: the particles of the flocculant are adsorbed on the dispersed particles and on coagulant flakes to convert them into particles of reasonably large size and high stability. The time required to clarify water is thus sharply decreased. The following substances are used as flocculants: starch, sodium polyalginate, polyacrylamide, a copolymer of vinyl acetate and maleic anhydride, activated silica, etc.

*Polyacrylamide.* This is a widely used thickening agent



Small quantities of this additive (up to 1 mg/litre) accelerate 10-20 times coagulation by aluminium sulphate and reduce the consumption of coagulant 2-3 times.

According to H. Sontheimer, a flocculant interacts with a colloidal particle in two stages (Fig. 9.3, *a* and *b*). The polymer is first adsorbed on a colloidal particle. Only one end of the flocculant is fixed to the colloidal particle, while the other end remains in the solution. Then two particles, with the flocculant molecules adsorbed on them, join together. The polymer becomes a bridge between the two particles. The interaction is fast and occurs simultaneously throughout the entire volume of the system. But if repulsion forces arising inside a floccule are greater than the attraction forces, it breaks down as shown in Fig. 9.3*b* by the sign of reversibility.

The polymer must not attach itself on one particle with both its ends because flocculation will then not occur (Fig. 9.3*c*). Excess

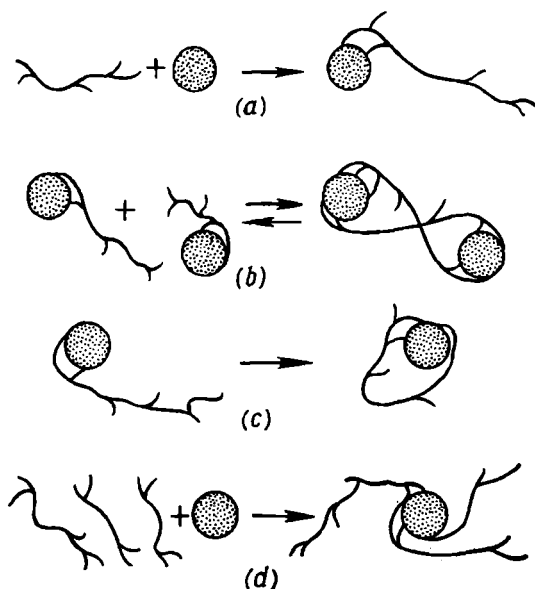


Fig. 9.3. Processes occurring in flocculation (after H. Sontheimer):

**a**—interaction between a polymer and a colloidal particle under optimum conditions; **b**—formation of floccules and their possible destruction due to internal repulsive forces; **c**—double adsorption; inactive particle (restabilization); **d**—excess polymer (stabilization)

flocculant can loosen the floccule structure (9.3d). Soviet scientists explain this phenomenon as resulting from the formation of a stable spatial reticular structure from adsorbed macromolecules of the flocculant which precludes the process of the enlargement and precipitation of suspended matter.

The interaction of polyacrylamide with clay particles and metal hydroxides is due to the interparticle van der Waals forces and the hydrogen bond formed between the polymer amide groups ( $-\text{NH}_2$ ) and the oxygen of aluminosilicates ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) or metal hydroxides. This explains the stability of the flakes that are formed.

Polyacrylamide (PAA) accelerates the coagulation of particles whose aggregation state is unstable. It is added to water pretreated with mineral coagulants. When turbid waters containing coarse suspended particles are treated, PAA is added without any mineral coagulants (or added before the coagulant). The time when PAA should be added is determined empirically. The effectiveness of the PAA dose depends on the method of application, the quality of the treated water, and type and size of the water treatment plant.

If PAA is added to the water before it enters the filter and the contact clarifying unit, the dose should be selected empirically for a given plant, depending on the quality of the filtrate, the filtration rate, and the consumption of washing water.

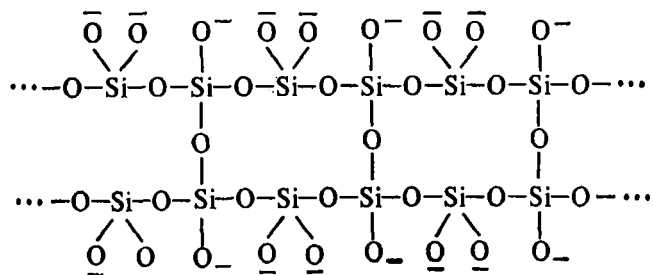
If PAA is added to the water before it enters the first stage units (settling tanks, clarifying tanks with suspended sludge), the dose is determined by test flocculation, by the clarifying effect produced on the water. PAA does not alter the taste of water or its pH.

Polyacrylamide accelerates flocculation and precipitation of suspended matter to clarify water; it intensifies the filtration in clarifying units with suspended sludge by increasing the height of the filtration bed with the retained stable flakes; it decreases the residual concentration of the coagulant in the purified water and decreases the coagulant dose during winter.

Industrial polyacrylamide is a clear yellow-green gel containing from 4 to 9 per cent of active agent, that is, polymer, whose macromolecule consists of acrylamide units and salts of acrylic acid. It also contains gypsum or ammonium sulphate as impurities, and small quantities of the monomer. When exposed to air, polyacrylamide loses its water to change into thin, brittle platelets. It is recommended that polyacrylamide be kept in closed containers at positive temperatures.

Aqueous solutions of industrial PAA do not appreciably corrode equipment and can be kept for 20 days.

*Activated silicic acid.* Activated silica (AS) is prepared at water treatment plants from soluble glass and a mineral acid\*. The activating agent neutralizes the alkalinity of soluble glass and liberates meta-silicic acid, which on contact with water becomes ortho-silicic acid  $H_4SiO_4$ . Ortho-silicic acid is polycondensed to form negatively charged colloidal particles in water



This process takes time, and a solution of activated silicic acid is therefore used to treat water only after the colloidal-disperse system has been ripened for 90-120 minutes. This flocculant promotes coagulation of positively charged particles (e.g. ferric hydroxide, aluminium hydroxide, etc.). The optimum doses of flocculants and when to

\* 40 ml of  $H_2SO_4$  (density, 1.165 g/cc) are used for each litre of a 5 per cent solution of  $Na_2SiO_3$ , which corresponds to a 22-23 per cent concentration of  $H_2SO_4$ .

use them are determined experimentally by test coagulation. As a rule, the optimum dose does not exceed 10 mg/litre of  $\text{SiO}_2$  (more often from 3 to 6 mg/litre).

Beside mineral acids, other agents are also used to activate silicic acid. These are, for example, aluminium sulphate, chlorine, carbon dioxide, ammonium sulphate, and others. The selection of the activating agent depends on the capacity of a given water treatment plant and on economic considerations. All activating agents give negatively charged colloidal particles.

The intensifying action of AS on processes of coagulation, sedimentation, and filtration is usually explained by the mutual coagulation of oppositely charged colloidal particles of silicic acid and aluminium hydroxide. Coagulation can also be accelerated because the colloidal particles of activated silicic acid are centres of growth of the coagulating sol particles. Activated silicic acid has many advantages over many other intensifying agents. It is very simple to prepare and costs less than other flocculants. Another advantage of activated silicic acid is that it can widen significantly the range of effective doses of the coagulants and of the pH range within which the coagulation process is effective.

Flakes formed by activated silicic acid additives are better retained by the filter to increase the working cycle of the filter packing and its capacity. Large grain materials can therefore be used, which increases the rate of filtration.

**Flocculant BA-2.** This is a cation-type high molecular water-soluble polyelectrolyte with a positively charged macroion (for which reason it can flocculate negatively charged suspensions without any mineral coagulants). It is *nontoxic*.

It probably works through the mutual neutralization of the oppositely charged particles of the suspension and the flocculant. Excess flocculant BA-2 worsens the purification of water from suspensions, which indicates that the colloidal particles are recharged (peptization).

Liquid clarification with flocculants is markedly accelerated, especially when the water temperature is low and when the coagulation process is very slow or is absent altogether.

Experiments show that flocculants can significantly intensify the work of water treatment plants and so lessen their size.

**Electrochemical Coagulation.** This is achieved by passing water between aluminium plates spaced 10-20 mm from one another.

The principle of operation is the anode dissolution of aluminium or iron plates when direct current is applied to them. To that end, one aluminium plate is connected to the positive and one to the negative pole of a powerful source of low voltage. Aluminium ions pass into the water to form aluminium hydroxide.

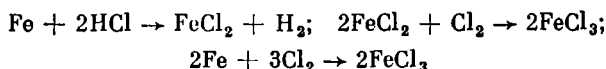
The advantage of this method is that stable flakes are quickly formed and precipitated and also that the pH of the medium does not need

to be changed. A disadvantage of the method is high energy consumption. To save electricity it is recommended that the current density should not exceed 10 A/sq. m, the distance\* between the electrodes should not exceed 20 mm, the flow rate of water between the electrodes should be not lower than 0.5 m/sec, and that the electrode potential should be changed periodically or the electrodes should be rotated.

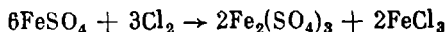
If iron is used as the anode in the electrolyzer, it is dissolved and sends divalent iron ions into the water. To remove iron from the water as  $\text{Fe}(\text{OH})_3$ , an oxidant should be present (dissolved oxygen or active chlorine). The relatively high cost of this method imposes certain limitations on its use and it is most efficient in small-capacity plants or when water is being treated for special purposes in the absence of the ions  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ .

**Coagulants.** Aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3$ , and ferric chloride,  $\text{FeCl}_3$ , are most commonly used as coagulants. A disadvantage of aluminium sulphate is its sensitivity to the temperature of the water to be treated. At low temperatures aluminium hydroxide forms a strongly hydrated and therefore very stable sol. The increased stability of the sol affects the process of flocculation, and this means high coagulant consumption in winter.

Ferric chloride is the most important of the iron-containing coagulants. It is prepared at water treatment plants by the action of chlorine water on iron chips. The following reactions occur:



Ferrous iron is used as a coagulant when it is added to chlorine ( $\text{Cl}_2 + \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), in the ratio by weight of 1 : 8. The substances react as follows:



Coagulation is especially effective with subsequent liming.

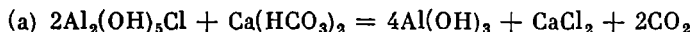
Unlike aluminium coagulants, iron-containing coagulants are not sensitive to temperature and pH changes. They can therefore be used with waters of various compositions. Moreover, precipitation with iron coagulants is faster than with aluminium coagulants, because the density of  $\text{Fe}(\text{OH})_3$  flakes is greater than of  $\text{Al}(\text{OH})_3$  flakes ( $d_{\text{Fe}(\text{OH})_3} = 3.6$  and  $d_{\text{Al}(\text{OH})_3} = 2.4$ ). But the bulk of large flakes precipitate very quickly, while smaller ones remain in solution for a long time, and so deteriorating the quality of the water. Mixed coagulants, consisting of aluminium sulphate and ferric chloride (1 : 1), are therefore used. Colloidal aluminium hydroxide is adsorbed on ferric hydroxide during coagulation, and they are mutu-

\* The distance between the metal plates should not be less than 10 mm, otherwise they could come into contact and the interelectrode gap would be clogged with suspended pollutants.

ally flocculated and precipitated. The mixed coagulant has all the positive properties of an iron-containing coagulant. At the same time flocculation is more uniform and the clarification is more complete. Mixed coagulant saves aluminium sulphate in the winter (up to 60-65 per cent). It is usually used for the coagulation of industrial effluents.

In addition to these coagulants, 5/6 aluminium oxychloride ( $\text{Al}_2(\text{OH})_5\text{Cl}$ ) is also used. A molecule of this reagent contains three times as much aluminium as aluminium sulphate. The salt content of water treated with this reagent is markedly less than that treated with aluminium sulphate. The coagulant does not require alkalyzing because it reduces the alkalinity of water less than  $\text{Al}_2(\text{SO}_4)_3$ .

When we compare the two reactions:



we see that the amount of liberated  $\text{CO}_2$  is six times greater in reaction (b) than in reaction (a). Carbon dioxide increases the acidity of water and so it requires additional alkalyzing.

### 9.3. Disinfection of Water

Coagulating and filtering water through sand purify it from suspended solids and partly decrease its bacteriological contamination. Complete disinfection is attained by chemical reagents which kill pathogenic microorganisms. Chlorine gas and chlorine compounds, such as chlorinated lime, chloramines, chlorine dioxide, hypochlorites, as well as ozone, and salts of heavy metals are effective against microorganisms. Ultra-violet radiation, ultrasound and other physical factors also kill pathogenic organisms. But the most common disinfecting agent used to treat water is chlorine and chlorine compounds.

**Disinfection with Chlorine and Chlorine Compounds.** The disinfecting action of chlorine and its compounds depends on the oxidation-reduction processes occurring in microbial cells subjected to the influence of these chemicals. We suppose that hypochlorous acid reacts with bacterial enzymes to interfere with the metabolism inside the cell.

Free and bound active chlorine have different oxidation potentials (see the electrochemical series); the reaction rate and the required contact time are also different. Hypochlorous acid is the most effective chlorine compound.

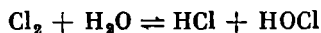
The effectiveness of chlorine against microbes depends on the initial dose of chlorine, the time it is in the water, and the pH of

the water. Chlorine is consumed to oxidize organic and mineral impurities in water. A lot of chlorine is required if the water is treated without preliminary settling. Chlorine is adsorbed on suspended matter, while microbes inside the floccules or large suspended particles remain intact.

Organic impurities in water are destroyed with chlorine. For example, humins are mineralized to  $\text{CO}_2$ , ferrous iron is oxidized to ferric iron, divalent manganese is oxidized to tetravalent manganese, and stable suspensions are converted into unstable ones due to the decomposition of the protective colloids. Sometimes, plant and animal organisms destroyed by chlorine in the water are converted into decay products with a strong odour. Chlorination of water containing phenols and other aromatic substances gives an especially unpleasant and stable odour. Smack and odour develop in water containing quantities of phenols as small as 1 : 10,000,000. They strengthen with time and do not disappear on heating. Large doses of chlorine are sometimes used to destroy aromatic compounds.

Chlorination is very important for the purification of fine disperse particles from water. It discolours water and provides good conditions for clarification and filtration.

When dissolved in water, chlorine forms two acids, viz., hydrochloric and hypochlorous:

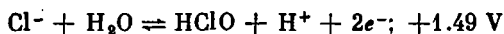


Hypochlorous acid is very weak and its dissociation depends on the pH of the medium.

*Dissociation of HOCl in water at various pH (20°C)*  
(according to Y. Y. Lurie)

pH	4	5	6	7	8	9	10	11
OCl <sup>-</sup> , %	0.05	0.5	2.5	21.0	75.0	97.0	99.5	99.9
HOCl, %	99.95	99.5	97.5	79.0	25.0	3.0	0.5	0.1

Hence, the lower the pH of the system, the higher the concentration of hypochlorous acid, which disinfects water due to its high redox potential

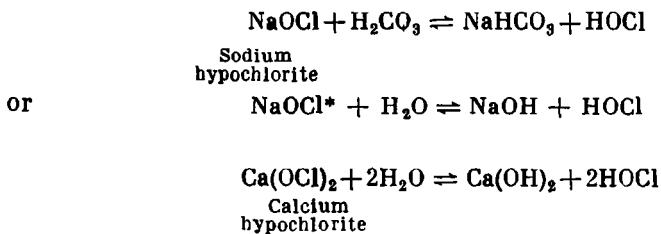


Therefore water should be disinfected with chlorine and its derivatives before alkali reagents have been added to it.

When chlorine compounds are added to water they are hydrolyzed to give hypochlorous acid, for example:



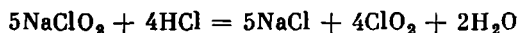
Chlorinated  
lime



True, the hydrolysis of salts is slower than of free chlorine, and the formation of HOCl is therefore slower as well. But the further action of hypochlorous acid is the same as the dissolution of chlorine gas in water.

Chlorine dioxide is of particular interest for water chlorination procedures. Its advantage over chlorine is that  $\text{ClO}_2$  oxidizes phenols to quinone and maleic acid, which do not give off the unpleasant chlorophenolic odour.

Chlorine dioxide is prepared by various methods, for example, by the action of hydrochloric acid on sodium chlorite



In selecting a method of disinfection the content of active chlorine in the disinfecting agent should be taken into account. *The quantity of molecular chlorine corresponding to the oxidative power of a given compound with respect to potassium iodide in an acid medium is called active chlorine.*

Each pair of electrons accepted by the oxidant is equivalent to 71 carbon units of free chlorine. Therefore, the compounds  $\text{Cl}_2$ , NaOCl,  $\text{CaCl}_2\text{O}$ ,  $\text{NH}_2\text{Cl}$ ,  $\text{H}_2\text{O}_2$  correspond to 71 parts by weight of active chlorine, and the compound  $\text{NHCl}_2$  to 142 parts.

The concept "active" chlorine describes the oxidizing power of a compound (with respect to potassium iodide in an acid medium) rather than the actual chlorine content of a given compound. For example, a gram-molecule of NaCl contains 35.5 g of chlorine, but the active chlorine content is zero. The actual chlorine content of a gram-molecule of NaOCl is 35.5 g, and the active chlorine content is 71 g.

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\* If chlorine is not available in sufficient quantities, or if the water treatment plant is of small capacity, sodium hypochlorite can be used to disinfect water. This reagent can be obtained by the electrolysis of an aqueous solution of sodium chloride. When the salt solution is electrolyzed in an apparatus without a diaphragm, the products of the electrolysis react with each other to give sodium hypochlorite:



This method is however not efficient because the energy consumed to prepare 1 kg of NaOCl is 6.5-7 kW·h under optimum conditions. The consumption of salt is 6-8 kg.

The following formula can be used to calculate the active chlorine content of chlorine compounds (in per cent):

$$\%Cl_2 = (nM : M_0) 100$$

where  $n$  is the number of hypochlorite ions in a molecule of a chlorine compound;  $M_0$  is the molecular mass of a chlorine compound; and  $M$  is the molecular mass of chlorine.

Determine the active chlorine content of chlorinated lime of the following composition:  $3CaOCl_2 \cdot Ca(OH)_2 \cdot 5H_2O$

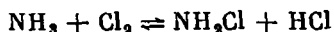
$$[Cl_2] = \frac{3 \times 71 \times 100}{545} = 39.08\%$$

When determining the chlorine dose, one should proceed from the chlorine-absorbing power of water plus a certain excess of chlorine ensuring the necessary *bactericidal* effect.

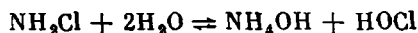
The functional dependence of chlorine absorption in water on the chlorine concentration is found by experiment. To that end, various doses of chlorine are added to a sample of water and its concentration is measured after a lapse of time (usually 30 minutes). A chlorine absorption curve is constructed with the data obtained (Fig. 9.4).

If the chlorine dose is small, the residual chlorine concentration is zero. When the chlorine dose increases residual chlorine is revealed in the water, and at certain levels the residual chlorine concentration becomes proportional to the concentration of the chlorine added minus the constant  $a$ . When the curve straightens out, it indicates that all oxidation processes which can be produced in water by chlorine have been completed. If we now continue the straight line until it intersects the  $x$ -axis, it will cut off a line  $OA$  representing the full chlorine absorption of water.

In order to preclude chlorophenolic odour and smacks in chlorinated river water containing phenol, it is recommended that *ammoniation* should be combined with *chlorination*. This method means adding ammonia or ammonium salts to the water. Chlorine reacts with them in the water to form chloramines:



Chloramines are gradually hydrolyzed in water to give  $NH_4OH$  and  $HOCl$ :



The slow hydrolysis of chloramine ensures a gradual supply of  $HOCl$  to the water and a more effective bactericidal action.

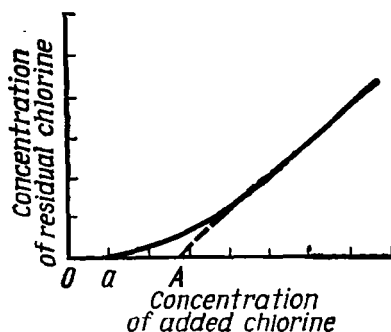


Fig. 9.4. Chlorine absorption curve

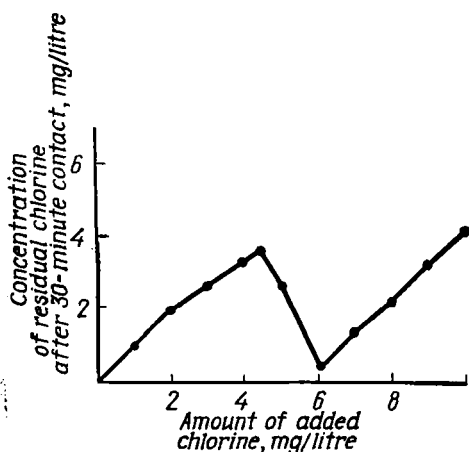
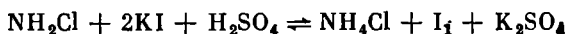


Fig. 9.5. Chlorine absorption in water in the presence of ammonia ion

The chlorine absorption curve is different for waters containing ammonia or its salts (Fig. 9.5), because chlorine reacts with the nitrogen compounds to give chloramine. When residual chlorine is determined iodimetrically, chloramine (like free chlorine) liberates iodine from potassium iodide:

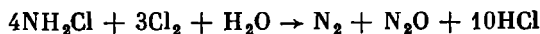


Chloramine is hydrolyzed more slowly than free chlorine, and the residual active chlorine content first increases until it reaches a maximum, when other chemical reactions begin in the system and it decreases (minimum on the curve).

Explanations of this minimum are controversial. Some authors maintain that it is due to the mutual oxidation of di- and monochloramines



Others think that the minimum is due to the interaction between monochloramine and chlorine\*\*



Both processes are possible from the standpoint of covalent bond theory, provided the nitrogen of the dichloramine has a polar bond with excess positive charges, because electronegative chlorine attracts electrons more strongly than nitrogen. What is indisputable

\* In order to bind excess chlorine in chloramines, it is recommended that ammonia be added in two stages. The major part should be added before the chlorine and about 0.1 mg/litre should be added at the end of the chlorination. This is important to remove the smell of the residual chlorine.

\*\* See Clair N. Sowyer, Kulsky, L. A., and Lebedintseva, O. K.

When water is treated by chlorination with ammoniation, first ammonia and then chlorine are added\*. The chlorine dose is determined by test chlorination so that the residual chlorine content of the water after 30 minutes should not be lower than 0.3 and not higher than 0.5 mg/litre.

To obtain monochloramine, 5.07 mg of chlorine are theoretically required for each milligram of ammonium nitrogen. But in practice, 5-6 mg of chlorine are used.

is that the minimum on the curve is due to redox processes leading to the destruction of chloramines and liberation of chlorine gas\*.

The treatment of water with chlorine in doses smaller than those corresponding to the minimum on the curve is called *chlorination before the break point*, while the treatment with larger doses is called *chlorination beyond the break point*. Potable water is usually chlorinated with small doses, but sewage receives large doses, beyond the break point, when the chloramines are destroyed completely. But if water contains aromatic substances, it acquires an unpleasant chlorophenolic odour. The odour begins to develop at the point when chlorine stops binding into the chloramines. The latter do not react with aromatic hydrocarbons and do not therefore impair the organoleptic properties of the water.

Treatment with chloramines is slower than with free chlorine; the water and the chloramines must be in contact not less than two hours.

Chlorine consumption during chlorination with ammoniation is the same as for treatment with chlorine alone. But chloramines are good for disinfecting water containing large quantities of organic matter, because the chlorine requirements are much lower in this case.

If water is chlorinated as a last stage after all other possible treatments have been given to the water we refer to *post-chlorination*.

*Pre-chlorination* is chlorination with large doses. Water is pre-chlorinated when normal chlorination impairs its organoleptic properties. The residual chlorine content of the water should be from 1 to 10 mg/litre.

*Periodical pre-chlorination* is used to treat cooling water at heat-and-power plants. One chlorination period is from 3 to 30 minutes. The interval between the introduction of chlorine doses varies from ten minutes (for a 3-minute chlorination period) to several hours (for 30-minute cycles). This treatment prevents the growth of micro-organisms which clog condensers.

But chlorination does not ensure complete sterilization of water and single viable organisms remain in it. Higher chlorine doses and a long contact of the water with the gas are therefore required to kill the sporeforming bacteria and viruses.

**Disinfection of Water by Iodine.** Water in swimming pools is iodinated. A saturated iodine solution in water is used. The concentration of the solution increases with temperature. For example, at 1°C the solubility of iodine in water is 100 mg per litre, at 20°C 300 mg/litre, and at 50°C 750 mg/litre.

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\* Indirect calculations of the thermodynamic potentials of these processes have shown that both processes are thermodynamically possible but the probability of the second process is three times as great as of the first one.

At pH less than 7, the iodine dose for the disinfection of water from natural sources varies from 0.3 to 1 mg/litre. The odour of iodine cannot be smelled because it can be sensed only at concentrations over 1.5 mg/litre. If the water contains chloramines, iodic acid (due to its lower oxidizing power) remains inactive till the moment when a strong oxidant is exhausted. This prolongs the time of the bactericidal action of iodic acid.

Water can also be disinfected by organic iodine compounds, *iodophores*.

**Ozonization of Water.** The bactericidal action of ozone has been known since late in the last century but it was only early in this century that ozone actually began to be used for treating water. In 1911, at that time the largest filtration station in the world was put into operation in St. Petersburg. Its capacity was 50,000 cubic metres of drinking water per day. World War One interfered with the normal work of this ozonizing unit; it was closed and drinking water was chlorinated instead.

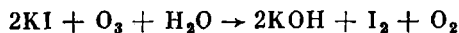
The high technological indicators given by ozonization offer good prospects for its practical use in the treatment of water. Ozonization units are known to be under construction in many countries, e.g. in the USA, France, Switzerland, Italy, Canada, and others.

An enormous amount of work on the ozonization of water from the Neva, Volga, Dnieper, and other large rivers of the USSR has been carried out over recent years.

Ozone is an allotropic modification of oxygen. Under normal conditions it is a bluish gas. When in the liquid state, ozone is dark blue and in the solid state, almost black. Its boiling point is minus 111° and melting point minus 250°C. It can be detonated in any state of aggregation. Its solubility in water is higher than that of oxygen.

Small concentrations of ozone in the air are beneficial to man, especially in respiratory pathology. But ozone becomes harmful when concentrations reach relatively high levels. Prolonged exposure to ozone (in the air in a proportion of 1 : 1,000,000) causes irritability, headache and fatigue. At higher concentrations nausea, nasal bleeding, and inflammation of the eye mucosa develop. Chronic ozone poisoning results in serious illness. The maximum allowed concentration of ozone in industrial air is 0.1 mg/cu. m.

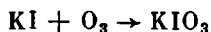
Ozone can be detected qualitatively by a red litmus or starch paper impregnated with a KI solution. The ozone reacts as follows:



Both types of paper turn blue on exposure to ozone: from KOH in the case of the litmus paper, and from molecular iodine in the case of the starch paper.

Ozone is determined quantitatively by passing a specified volume of gas through a KI solution containing borax (to ensure a weak al-

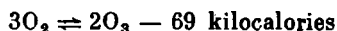
kaline reaction). Ozone is completely bound in these conditions:



It is determined by the quantity of potassium iodate formed in the reaction.

In nature, ozone is formed by discharges of atmospheric electricity during storms and by oxidation of a number of organic substances. Appreciable amounts of ozone are contained in the air in coniferous forests, where conifer resin is oxidized. The coastal areas are also rich in ozone which is liberated by the oxidizing of seaweed thrown up onto the shore.

Oxygen is oxidized to ozone according to the following equation:



The thermochemical equation shows that ozone is formed with the absorption of heat. Hence its molecule is unstable and can decompose spontaneously, since the decomposition process is accompanied by the liberation of heat. This explains the higher activity of ozone compared with molecular oxygen.

Air-ozone or ozone-oxygen mixtures containing more than 10 per cent of ozone, are explosive. But the same mixtures containing smaller quantities of ozone are stable under a pressure of a few atmospheres. They are heat and shock-resistant, and react stably with traces of organic impurities. However pure ozone will explode violently at the slightest disturbance.

The decomposition of ozone is accelerated by heating. It decomposes more slowly in dry air and faster in water, and very rapidly in strongly alkaline solutions; it is relatively stable in an acid medium. Experiments show that 60 per cent of 2.5 mg of ozone dissolved in 1 litre of distilled water is decomposed in 45 minutes.

The solubility of ozone in water (like all other gases) depends on temperature and on its partial pressure over water. For the practical determination of ozone solubility at a given temperature we often use the coefficient ( $R_t$ ) of its distribution between the air and the liquid phases at that temperature:

$$R_t = \frac{\text{Amount of } O_3, \text{ in mg, dissolved in 1 l of water at } t^\circ\text{C}}{\text{Amount of } O_3, \text{ in mg, contained in 1 l of air phase at } t^\circ\text{C}}$$

If the distribution coefficient is known, one can calculate the possible ozone concentration in water at equilibrium.

The value of the distribution coefficient changes with temperature. For example, at  $0^\circ\text{C}$  it is 5, and at  $25^\circ\text{C}$  it is 2.4.

The solubility of ozone in natural waters depends on the pH of the medium and on the presence of dissolved matter in water. For example, the presence of calcium sulphate or of small amounts of acid increases the solubility of ozone, while an increased alkali con-

tent decreases its solubility. Hence it is necessary to control the pH of the medium during ozonization of water (the pH should be neutral).

The bactericidal action of ozone is associated with its high oxidation potential and the ease with which it passes through the cell membranes of microbes. Ozone oxidizes the organic substances in the microbe cell in order to kill it.

Owing to its high oxidation potential (2.076 V), ozone has a stronger bactericidal action than chlorine (1.36 V). It works on bacteria more quickly and the amount of gas is less.

For example, the poliomyelitis virus is killed within two minutes of exposure to 0.45 mg/litre of ozone, while chlorine takes three hours at a concentration of 2 mg/litre.

Experiments show that if one millilitre of water contains 274-325 bacteria of *E. coli* type, 86 per cent are killed by an application of 1 mg/litre ozone, while 2 mg/litre ozone fully disinfects the water. Sporeforming bacteria are more resistant to ozone than nonsporeforming but they are resistant to chlorine as well.

Ozone is detrimental to the hydrobios. A dose of 0.5-1.0 mg/litre kills aquatic plants. About 90 per cent of dreissensia larvae are killed by 0.9-1.0 mg/litre, and a dose of ozone of about 3 mg/litre fully disinfects water. Leeches are very sensitive to ozone and are killed by about 1 mg/litre concentration. A dose of 2 mg/litre kills cyclops, oligochetes, daphnia, and rotifers.

Chironomids and water mites are highly resistant to ozone (up to 4 mg/litre), but they are not killed by chlorine either.

The dose of ozone required for water disinfection depends on the degree of pollution, but usually varies from 0.5 to 4.0 mg/litre. The consumption of ozone increases with water turbidity and higher doses are required for turbid waters. The disinfecting action of ozone almost does not depend on the temperature of the water.

Ozonization not only decontaminates water but also gives it a pleasant taste, lowers its colour, and kills off odour produced by oxidation and mineralization of organic impurities. For example, humins are completely broken down by ozone to give carbon dioxide and water.

The ozonization of water has some advantages over chlorination:

(1) it improves the organoleptic properties of water and does not add to its chemical pollution;

(2) ozonization does not require additional processes to remove excess bactericidal agents from purified water (as is the case with dechlorination); hence higher doses of ozone can be used;

(3) ozone can be prepared in situ. Only electricity is required, and a single chemical reagent, silica gel, on which moisture is adsorbed from the air.

In industry ozone is prepared by passing dry and clean air through an ozonizer under constant pressure, where it is subjected to an elec-

tric discharge (a silent discharge). The ozonized air is then mixed with water in special chambers. Modern equipment is provided with bubblers and jet-ejectors.

Ozonization of water is not widely used because of the complexity of ozone manufacture and the large amounts of high frequency and high voltage electricity is required.

Ozonization of water is also complicated by the fact that ozone is a corrosive agent. The gas and its aqueous solutions destroy steel, cast iron, copper, rubber, and ebonite. All apparatus for the manufacture of ozone, and the pipes through which its solutions pass should be of stainless steel or aluminium. Stainless steel can withstand the corrosion for 15-20 years and aluminium for only 5-7 years.

Ozonization of water will be profitable only if a suitable material is found, electric energy is cheap, and the method of bringing water in contact with ozone is improved. Then ozonization will enjoy a wider use, especially in cases where, in addition to disinfection of water, its colour, taste and odour also need to be improved.

**Disinfection of Water by Silver Ion (Oligodynamics).** The bactericidal action of silver has been known since time immemorial. Water and wine used to be kept in silver vessels in order to retain their quality over long periods of time.

There are a few hypotheses explaining the bactericidal action of silver. According to one of them, the silver ion interferes with the metabolism of bacteria and thus kills them. According to another hypothesis, the silver ion penetrates inside the microbial cell and destroys its protoplasm. There also exists an opinion that the silver ion is adsorbed on a microbial cell and acts like a catalyst to accelerate the oxidation of plasma by the oxygen of the air.

It is quite possible that all these factors are involved. What is indisputable is that chemical processes are mainly responsible for the disinfecting effect of silver on water. This opinion is confirmed by the fact that the efficiency of the disinfecting effect of the silver ion increases with the concentration of the ion and with the temperature of the water. The rate of a chemical reaction is known to accelerate with increasing concentration of the reactants and with increasing temperature. The higher temperature intensifies the dissociation of the silver salts and decreases the activation energy of the system. Take as an example a sample of water infected with *E. coli* bacteria. When the water is heated from 0 to 10°C and treated with the silver ion for thirty minutes, the disinfecting effect increases four times, while with a rise in temperature to 42°C the same dose of the silver ion ensures the complete purification of the water from microorganisms in an even shorter time.

Water can be disinfected with silver metal. The silver ion concentration grows if the contact surface increases. In order to ensure the maximum surface of silver with the least possible expenditure of

metal, it is precipitated in a thin layer onto a material in a form with a well developed surface, such as sand, rings, beads, etc., through which water is passed.

Theoretically, a relatively insoluble silver salt AgCl containing about  $1 \times 10^{-5}$  g-ion/litre of the silver ion in a saturated solution, might be a better disinfecting agent since the lower limit of the bactericidal action of silver is estimated to be  $2 \times 10^{-11}$  g-ion/litre. But it is difficult to work with AgCl precipitate since it forms a saturated solution only in the vicinity of each solid particle. If the salt is thoroughly mixed with water, additional apparatus is needed to retain the suspension.

The electrochemical dissolution of silver (anodic dissolution) is used in water treatment. This method can be used to accurately control the silver dose and the disinfecting process.

Silver water prepared electrochemically has a stronger bactericidal action than chlorine (L. A. Kulsky). If silver is added to water infected artificially with various bacteria in the quantity of 1 mg/litre the water is completely disinfected in two hours. All bacteria can be listed in order of their increasing resistance to silver: staphylococci, streptococci, typhoid bacteria, dysentery bacteria, *E. coli*. *E. coli* have the highest resistance to silver and it is therefore used as an indicator of water purity. If *E. coli* are found in water after treated with silver it indicates that all other pathogenic bacteria might also be present in the water.

The bactericidal action of silver is affected by the presence of various impurities in natural waters. They can bind the silver ion into complexes, adsorb it on suspended particles, and thus deteriorate the conditions for contact. For example, an increased chloride ion content of water can decrease the solubility of relatively insoluble salt AgCl. The disinfection of water by silver ions can thus be hindered by the presence of large quantities of chloride ions. For example, most clear waters containing from 5 to 25 mg/litre of chlorides require from 0.05 to 0.20 mg/litre of silver. Waters containing more chlorides require silver in higher doses.

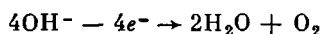
Silver is batched into water by special devices called ionators\*.

When water from a new source is treated with silver, its dose should be established experimentally, since it depends on the salt composition of each particular water. Impurities contained in water often change the electrode potentials, due to the physico-chemical changes occurring at their surfaces (galvanic polarization). For example, if the chloride ion concentration in water is 250 mg/litre, AgCl precipitates on the electrodes and interferes with the transfer

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\* L. A. Kulsky has worked out an LK-type automatic ionator to prepare silver ions. This apparatus is described in detail in his books *Chemistry and Water Treatment*, 1960; *Fundamentals of Physico-Chemical Methods of Water Treatment*, 1962 (in Russian).

of the silver ion into the solution. Salts with oxygen-containing ions, such as  $\text{SO}_4^{2-}$ , also interfere with the electrolytic dissolution of silver. In their presence, the hydroxyl is discharged at the anode to form water and oxygen:



Other oxygen-containing anions, such as  $\text{PO}_3^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{NO}_2^-$  give sparingly soluble silver salts, which have the same effect on the electrodes as the chloride ion.

"Silver water" is prepared separately and then added to the treated water. This method is used to disinfect water in sanatoria, hospitals, on board ships, etc. This water can be used to can foods, to treat artesian and common wells, pipes, and also for medicinal purposes.

The silver treatment of water is only effective in cases where the water does not contain much salt or suspended matter. Turbid waters are disinfected very slowly and the efficiency is low.

Copper also possesses oligodynamic properties. If a body of water is overgrown with aquatic plants, copper ions in the form of a soluble salt  $\text{CuSO}_4$  are used. Industrial water can be treated by electrolytic dissolution of copper.

**Disinfection of Water with Ultra-Violet Radiation.** The bactericidal action of ultra-violet radiation is explained by its effect on the protoplasm and the enzymes of microbial cells. Wavelengths from 2000 to 2950 Å have the strongest effect (this region of the spectrum is known as the bactericidal).

The ultraviolet rays kill the vegetative forms of bacteria, spores, protozoa, and viruses.

The efficacy of the irradiation depends on the bactericidal energy, on the amount of suspended matter, on the quantity of microorganisms and their morphological and physiological properties, and on the optical density of the water (or its absorbing power).

Bacteria are characterized by different resistivities to bactericidal energy. The criterion of bacterial resistance is the amount of energy required to stop the vital processes in the living microorganism in order to attain a given degree of water disinfection. This is determined by the ratio of the final amount of bacteria  $P$  to the initial quantity  $P_0$  in a unit volume:  $P/P_0$ .

Three ultra-violet radiation levels are distinguished from the physiological standpoint: (1) a dose which does not kill bacteria; (2) a minimum bactericidal dose killing a large proportion of a given bacteria; (3) a full bactericidal dose killing all the bacteria of a given species.

The minimum bactericidal dose (sub-bactericidal dose) of ultra-violet radiation stimulates the growth and propagation of species which would otherwise remain inactive. A longer irradiation kills the bacteria. For example, the study of typhus group cultures has

shown that ultra-violet irradiation for 0.017 to 0.17 seconds increases the number of colonies ( $\frac{P}{P_0} > 1$ ) up to 1.6 times. If the irradiation continues from 0.25 to 0.83 seconds, the relative number of colonies decreases ( $\frac{P}{P_0} < 1$ ), in some cases to 0.2-0.3 of the initial level. A five-second irradiation of objects kills all bacteria of some species.

*E. coli* have the strongest resistance to U-V rays of all typhus bacteria. Some of them are not killed even by a 5-second irradiation. *E. coli* can therefore be an indicator of the efficacy of the disinfection of water infected with pathogenic nonsporeforming bacteria. If water contains stable sporeforming bacteria (such as anthrax bacilli), the criterion for the irradiation dose should be resistance of sporeforming bacteria least sensitive to ultra-violet radiation.

The number of survivals after irradiation ( $P$ ) can be calculated by the formula  $P = P_0 e^{-\beta t}$ , where  $P_0$  is the initial quantity of the bacteria;  $\beta$  is the empirically found constant of bacterial mortality;  $e$  is the base of natural logarithms;  $t$  is the time of irradiation in seconds.

The absorption of bactericidal radiation in test water is described in terms of the absorption coefficient  $\alpha$  which is found in the Bouguer-Lambert-Beer equation:  $E = E_0 e^{-\alpha x}$ , where  $E$  is the radiation dose after passing through the absorbing layer,  $\mu\text{W}/\text{sq. cm}$ ;  $E_0$  is the received dose on the substance surface,  $\mu\text{W}/\text{sq. cm}^*$ ;  $x$  is the thickness of the absorbing layer,  $\text{cm}$ ;  $\alpha$  is the absorption coefficient of bactericidal radiation in water,  $\text{cm}^{-1}$ .

The value of the absorption coefficient  $\alpha$  depends on the wavelength and the properties of the absorbing substance; it does not depend on the layer thickness or the irradiation intensity.

For currents which receive the same initial irradiation  $E_0$  and which pass through layers of the same substance of thickness  $x_1$  and  $x_2$ , the residual irradiation will accordingly be  $E_1$  and  $E_2$ . Comparing these values we obtain the following  $E_1/E_2 = e^{\alpha(x_2 - x_1)}$ . Whence the absorption coefficient:

$$\alpha = \frac{\log \frac{E_1}{E_2}}{(x_2 - x_1) \log e}$$

Experiments show that the coefficient of bactericidal absorption increases particularly with colour of water, with its ferrous iron content and the concentration of suspended substances (even in small quantities, up to 9 mg/litre); to a lesser degree it depends on the concentration of calcium and magnesium salts (up to 21 mg-equiv/litre).

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\* Bactericidal radiation is a current of wavelengths of 2536 Å, in microwatts, falling upon a surface of 1 sq. cm. located at a distance of 1 m from the source of radiation in the plane parallel to the source axis.

Once the absorption coefficient of natural waters is known, it is possible to determine the maximum allowed depth of water that can be treated with radiation.

V. F. Sokolov suggests that the following coefficients ( $\alpha$ ) should be used for tentative and preliminary calculations in designing units for treating water with ultra-violet rays:

(a) for colourless, subsoil waters recovered from great depths,  $0.10 \text{ cm}^{-1}$ ;

(b) for spring water, soil, subterranean and infiltration waters,  $0.15 \text{ cm}^{-1}$ ;

(c) for purified water from surface sources, depending on the degree of purification, from  $0.20$  to  $0.30 \text{ cm}^{-1}$ .

For more accurate calculations, the value of the coefficient  $\alpha$  should be determined from physico-chemical data.

The bactericidal current  $F_\sigma$ , required to disinfect water with immersed and nonimmersed sources of radiation, can be calculated using the following equation:

$$F_\sigma = - \frac{Q\alpha K \log \frac{P}{P_0}}{1563.4\eta_n\eta_0} W$$

where  $Q$  is the amount of irradiated water. cu. m/hr;  $\alpha$  is the absorption coefficient,  $\text{cm}^{-1}$ ;  $K$  is the resistance coefficient of the irradiated objects,  $\mu\text{W}\cdot\text{s}/\text{sq. cm}$ ;  $P_0$  is the microbial content of the water before irradiation;  $P$  is the number of microbes after irradiation;  $\eta_n$  is the power coefficient of the radiation source;  $\eta_0$  is the utilization coefficient of the bactericidal radiation (in planning water treatment plants this should be assumed to be  $0.9$ , since quartz shells having  $2\text{-mm}$  thick walls absorb from  $1$  to  $11$  per cent of the bactericidal current emitted from the radiation source).

Mercury lamps manufactured of quartz or uviol glass are used as the source of ultraviolet radiation. The lamps are  $15\text{-}20$  cm long tubes with oxide electrodes. With the application of an electric current, mercury vapour emits a bright greenish-white luminous flux rich in ultra-violet rays.

High-pressure ( $400\text{-}800$  mm Hg) mercury-quartz lamps and also argon-mercury low-pressure ( $3\text{-}4$  mm Hg) lamps are used as well. The bactericidal effect of high-pressure lamps is relatively low, but this is compensated for by their power ( $1000$  W). Low-pressure lamps have about twice the effect of high-pressure lamps, but their electric power does not exceed  $30$  W and they can therefore be used only in small-capacity units.

Water from surface sources should be treated with ultra-violet rays only after it has passed all other stages of treatment and contains as few as possible impurities, since these increase its absorption coefficient.

Thus treated water does not change its physical or chemical properties. The taste of water also remains unchanged. The disadvantage of this method is the high cost and the possibility of subsequent infection.

**Water Disinfection with Ultrasound.** Oscillations at frequencies over 20,000 Hz, not usually perceived by man, are called ultrasound.

Ultrasound oscillations are obtained in industry by piezoelectrical and magnetostrictive methods.

The former method is based on the *piezoelectrical effect* by which the crystals of some substances are mechanically deformed when placed in an electrical field and thus produce ultrasound.

Quartz plates, cut from the crystal, are used as sources of ultrasonic frequencies. Plates of equal thickness and lapped to one another (as mosaics) and attached with adhesives between two thick steel plates to which an electric current is applied. Such a system is a powerful source of ultrasound.

The other method is based on the phenomenon of *magnetostriction*. When ferromagnetic bodies are magnetized, they change their linear dimensions and volume. The magnitude and sign of the effect depend on the strength of the magnetic field and on the angle between the direction of the field and the crystal axis (for single crystals). The first method has proved to be of greater efficiency.

Ultrasound kills animal and plant cells, protozoa, and microorganisms. The destructive effect depends on the intensity of the ultrasonic waves and on the morphology of the object in question.

The bactericidal action of ultrasound is connected with its ability to form minute cavities in water around objects, thus isolating them from the environment to produce around them a local pressure measured in tens of thousands of atmospheres, the phenomenon being known as *ultrasonic cavitation*. The sharp changes in the physical state of the liquid, occurring at the ultrasound frequency, destroy substances inside the ultrasound field.

Bacteria are believed to be killed by the mechanical destruction of their cells by the ultrasound oscillations. The vital functions of the cells are disrupted mainly by the decomposition of the proteinous substances of the protoplasm.

Hydras, infusoria, cyclops, monogenetic flukes and other organisms are especially sensitive to ultrasound.

It has been established that ultrasound destroys larger organisms which are especially detrimental to the drinking and industrial water supply. These are organisms visible to the naked eye, such as the larvae of some insects (caddis flies, chironomids, may flies), oligo-chetes, some nematodes, sponges, Bryozoa, Dreissensia, leeches, etc. Some of them live in water treatment plants. Conditions permitting, they propagate and inhabit large areas. All these organisms are

killed by ultrasound. The fauna and flora of marine plankton are also killed by ultrasonic oscillations.

Laboratory experiments show that about 95 per cent of *E. coli* are killed by ultrasound in 1-2 minutes in thin layers of liquid. There are indications that ultrasound has a bactericidal effect on dysentery bacilli, typhus virus, etc. Milk can be sterilized by ultrasound.

**Thermal Disinfection of Water.** The most common method of disinfecting water has been known from time immemorial. It is boiling. Small quantities of water are disinfected by boiling nowadays. Drinking water is boiled in public catering establishments, at hospitals, various institutions, etc. But the method is expensive, it requires large vessels for boiling, and is not therefore used even in minor water supply systems. Furthermore, the thermal method fails to kill spores, and water taken from dubious sources will not necessarily be disinfected by boiling.

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## 9.4. Determining the Stability and Aggressiveness of Water

Water which does not change its composition after a prolonged contact with metal or concrete surfaces is known as *stable* water.

The stability of water can be reduced by the presence of carbon dioxide, low pH, oversaturation with  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ , and by increased concentration of sulphates and chlorides.

According to GOCT 3313-46, stable water does not liberate or dissolve calcium carbonate. The stability of water is described by the *stability index C*

$$C = \frac{A_{\text{in}}}{A_{\text{sat}}}$$

where  $A_{\text{in}}$  is the initial alkalinity of water in its natural state, mg-equiv/litre;  $A_{\text{sat}}$  is the alkalinity of water after mixing with calcium carbonate, mg-equiv/litre.

If  $C$  is less than unity, the water is aggressive; if greater than unity, it tends to precipitate calcium carbonate.

According to the same GOCT, water stability can be assessed by the ratio of pH in natural water and after contact with calcium carbonate:

$$C = \frac{\text{pH}_{\text{in}}}{\text{pH}_{\text{sat}}}$$

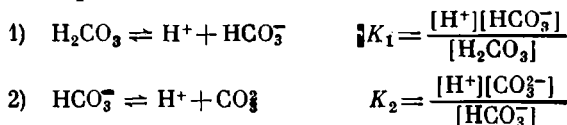
where  $\text{pH}_{\text{in}}$  is the pH of water in its natural state, and  $\text{pH}_{\text{sat}}$  is the pH of water after mixing with calcium carbonate.

If  $C$  is unity, the water is stable; if smaller than unity, it is aggressive; and if greater than unity, it can precipitate  $\text{CaCO}_3$ .

Carbon dioxide is one of the causes of water instability. Consider the forms in which it can occur in water.

**Carbon Dioxide and Its Forms.** The following forms of carbon dioxide are distinguished in chemical analysis: (1) total; (2) hydrocarbonate; (3) carbonate; (4) free; (5) equilibrium; and (6) aggressive.

The form of carbon dioxide can be determined by the dissociation constants of carbonic acid and the pH of the medium. Carbonic acid dissociates in steps:



The dissociation constants at  $25^\circ\text{C}$  are  $K_1 = 4 \times 10^{-7}$  and  $K_2 = 5.6 \times 10^{-11}$ .

Once the dissociation constants and the concentrations of any two ions in the equation are known, the concentration of the third ion can be determined.

The pH of the solution can be used to determine the ratio between the concentrations of the hydrocarbonate ion and carbonic acid, or the hydrocarbonate ion and the carbonate ion.

**Example 1.** Determine the ratio between the concentrations of  $\text{HCO}_3^-$  ion and carbonic acid,  $\text{H}_2\text{CO}_3$ , at pH 4 and  $25^\circ\text{C}$ .

**Solution.** Express pH through the concentration of the hydrogen ion ( $\text{pH} = -\log [\text{H}^+]$ ) and substitute the known values into the equation of the dissociation constant of carbonic acid (first stage dissociation):

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{K_1}{[\text{H}^+]} = \frac{4 \times 10^{-7}}{1 \times 10^{-4}} = 4 \times 10^{-3}$$

We obtain the ratio of the concentrations of the hydrocarbonate ion and carbonic acid at pH 4.

The solution of the problem shows that at pH 4 almost all the carbonic acid is in the free state (the denominator is almost 1000 times greater than the numerator).

**Example 2.** Determine the ratio between the concentrations of the ion  $[\text{CO}_3^{2-}]$  and the ion  $[\text{HCO}_3^-]$  at pH 12 and  $25^\circ\text{C}$ .

**Solution.** Substitute the known values into the equation of the dissociation constant of carbonic acid (second stage dissociation):

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{K_2}{[\text{H}^+]} = \frac{5.6 \times 10^{-11}}{1 \times 10^{-12}} = 56$$

Here the numerator is much greater than the denominator. Hence, at pH 12, almost all acid is in the form of the ion  $[\text{CO}_3^{2-}]$ .

**Example 3.** Determine the concentration of the ion  $[\text{HCO}_3^-]$  in water at pH 10 and the concentration of the ion  $[\text{CO}_3^{2-}]$  of 4 g-ion/litre.

**Solution.** The ion  $[\text{CO}_3^{2-}]$  is a part of the second dissociation constant of carbonic acid and it can therefore be used to solve the problem. Express the

active acidity through the hydrogen ion concentration ( $\text{pH} = -\log [\text{H}^+]$ ):

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{4 \times 10^{-10}}{[\text{HCO}_3^-]} = 5.6 \times 10^{-11}$$

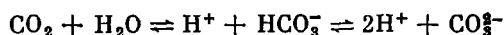
$$[\text{HCO}_3^-] = 0.071 \text{ g-ion/litre}$$

The form in which carbonic acid can be present in a given solution can be determined by titration of the solution in the presence of various indicators.

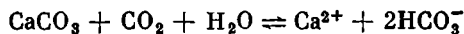
Free carbonic acid is determined by titration with sodium hydroxide in the presence of phenolphthalein (the point of equivalence at pH 8), and the hydrocarbonate and carbonate ions by titration with hydrochloric acid in the presence of phenolphthalein and methyl orange (the point of equivalence at pH 4).

The hydrocarbonate ion most frequently occurs in natural waters. Sometimes, its concentration is as high as 1200 mg/litre. The water of rivers and fresh-water lakes contains  $\text{HCO}_3^-$  not above 300 mg/litre. The  $\text{CO}_3^{2-}$  content of waters (except soda water) is small and depends on the solubility of calcium carbonate.

The  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions and carbon dioxide are equilibrated in solution by the carbon dioxide equation. This is the equilibrium of a system consisting of hydrocarbonate and carbonate ions and of free carbon dioxide:



The  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions are bound with the calcium ion in natural waters. Calcium carbonate is always present in calcium hydrocarbonate solutions in quantities not exceeding its solubility in water (the solubility product of  $\text{CaCO}_3$  at  $15^\circ\text{C}$  is  $9.9 \times 10^{-9}$  g-ion/litre, and its solubility is 9.95 mg/litre). In the presence of the calcium ion, the carbon dioxide equation is as follows:



If we apply the law of mass action to this equilibrium system, we get the following:

$$\frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CaCO}_3][\text{CO}_2][\text{H}_2\text{O}]} = K$$

The concentrations  $[\text{CaCO}_3]$  and  $[\text{H}_2\text{O}]$  are constants:  $[\text{CaCO}_3]$  expresses the concentration of a saturated solution of calcium carbonate, while  $[\text{H}_2\text{O}]$  the concentration of water molecules in solution. For this reason we join them to the constant and re-write the equation

$$\frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2]} = K[\text{CaCO}_3][\text{H}_2\text{O}] = K_{\text{CO}_2}$$

where  $K_{\text{CO}_2}$  is the carbon dioxide equation constant.

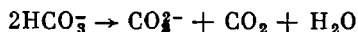
If we now express the calcium ion concentration through the hydrocarbonate ion concentration:  $[\text{Ca}^{2+}] = \frac{1}{2} [\text{HCO}_3^-]$  the equation

takes the following form:

$$\frac{[\text{HCO}_3^-]^3}{[\text{CO}_2]} = K_{\text{CO}_2}$$

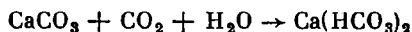
This equation shows that the hydrocarbonate ion can be present in solution only if free carbon dioxide is present as well. So the concentration of the hydrocarbonate ion is a function of the concentration of free carbonic acid.

If the concentration of  $[\text{CO}_2]$  is less than is required to maintain equilibrium, the hydrocarbonate ion will decompose according to the equation



until a new equilibrium is attained in the system.

If the concentration of  $[\text{CO}_2]$  is greater than is required to attain equilibrium,  $\text{CaCO}_3$  will dissolve



Hence, the *equilibrium*, or *inactive* carbon dioxide is that concentration of free carbon dioxide in which carbon dioxide should be present in solution in order to stabilize the hydrocarbonate ion (at a given concentration).

If the concentration of carbon dioxide is higher than equilibrium concentration,  $\text{CaCO}_3$  will dissolve. A carbonate film is formed on the surfaces of lime or concrete structures and they are corroded by the action of *aggressive* carbon dioxide. It is its presence which is responsible for the corrosive aggressiveness of such water. But aggressive carbon dioxide cannot be regarded as excess free carbon dioxide over equilibrium (inactive)  $\text{CO}_2$ . Excess quantities of free carbon dioxide act on calcium carbonate to convert it into a hydrocarbonate. The initial amount of the hydrocarbonate ion in solution is thus increased, and the concentration of the equilibrium carbon dioxide has to be increased to keep the new amount of the hydrocarbonate ion in solution.

It means that only part of the excess carbon dioxide will dissolve  $\text{CaCO}_3$ , while the remaining  $\text{CO}_2$  will pass into the equilibrium carbon dioxide to preclude the decomposition of the newly formed hydrocarbonate.

Hence, *the content of aggressive carbon dioxide is measured by the amount by which the concentration of free carbon dioxide decreases in water which has come into contact with the solid phase of calcium carbonate at the point where carbon dioxide equilibrium is attained.*

Aggressiveness of water is determined from the dissociation constant.

For dilute solutions at  $25^\circ\text{C}$ ,  $K_{\text{CO}_2} = 3.43 \times 10^{-5}$ . If  $\frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^3}{[\text{CO}_2]} = K_{\text{CO}_2}$ , the concentrations of the  $[\text{Ca}^{2+}]$  and  $[\text{HCO}_3^-]$  ions are ex

pressed in gram-ions per litre, while that of the  $[\text{CO}_2]$  in moles per litre. But if the concentration of  $[\text{Ca}^{2+}]$  and  $[\text{HCO}_3^-]$  is expressed in milligram-ions per litre, and of  $\text{CO}_2$  in millimoles per litre, the constant of carbon dioxide equilibrium is 34.3.

**Example.** Determine the stability of water if the  $[\text{CO}_2]$  content is 44 mg/litre,  $[\text{HCO}_3^-]$  122 mg/litre, and  $[\text{Ca}^{2+}]$  80 mg/litre.

**Solution.** Find the concentration of the equilibrium carbon dioxide by substituting all known values into the equation:

$$[\text{CO}_2] = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{34.3} = \frac{2 \times 2^2}{34.3} = 0.23$$

The water is aggressive toward concrete because the equilibrium concentration of  $\text{CO}_2$  is 0.23 mmole/litre, and the total amount of carbon dioxide contained in the water is 1 mmole/litre.

The dependence between the concentration of free and hydrocarbonate carbon dioxide can be shown graphically using the law of mass action (Fig. 9.6).

The points on the curve  $OK$  show the quantity of  $\text{CO}_2$  in equilibrium with the ion  $\text{HCO}_3^-$ . The points above this equilibrium curve correspond to aggressive waters, those below the curve to waters supersaturated with calcium carbonate.

If the amounts of free and hydrocarbonate  $\text{CO}_2$  in a sample of water are known, then, using the graph, one can establish the aggressiveness of the water. For example, in order to establish the concentration of aggressive carbon dioxide in a water sample whose composition corresponds to the point  $A$  on the curve, a right isosceles triangle  $ABC$  is constructed so that one of its apexes lies on the curve  $OK$ . The distance  $AC$  represents the amount of aggressive carbon dioxide.  $CD$  corresponds to the amount of equilibrium carbon dioxide, and  $OD$  to bound carbon dioxide.

Mixing together two nonaggressive waters whose compositions correspond to points  $M$  and  $N$  on the curve can produce an aggressive mixture, because its composition will depend on the curve  $MN$  lying above the equilibrium curve.

When the aggressiveness of a water sample is assessed, its salt composition should be taken into account along with the concentration of aggressive carbon dioxide, because the carbon dioxide equilibrium depends on the total salt content of water (the higher the salt content, the smaller the amount of carbon dioxide required to maintain the carbon dioxide equilibrium). The equilibrium is shifted, for example, during treatment of water by coagulation. The addition

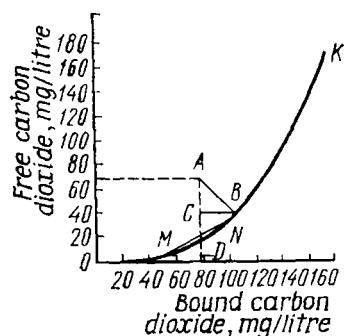


Fig. 9.6. Determining aggressive carbon dioxide in water

of 1 mg of anhydrous aluminium sulphate liberates 0.8 mg of carbon dioxide.

The dependence between free and bound carbon dioxide calculated by the law of mass action can be described in the form of a table (see Table 9.1).

**Calculating Aggressive Carbon Dioxide by Using Table 9.1.** The amounts of free and bound carbon dioxide are determined analytically (if the content of the hydrocarbonate ion is given in mg-equiv/litre, it should be multiplied by the equivalent weight of  $\text{CO}_2$ , i.e. by 22).

The total amount of free and bound carbon dioxide, in mg/litre, is found in column *S*, with the corresponding total of bound and aggressive carbon dioxide in column *G*. If we subtract the amount of bound carbon dioxide from the quantity in column *G*, we obtain the amount of aggressive  $\text{CO}_2$  contained in one litre of the water.

**Example.** An experiment showed that the water from an artesian well contained 4.70 mg-equiv/litre of hydrocarbonate ion and 50 mg/litre of  $\text{CO}_2$ . Determine the quantity of aggressive carbon dioxide.

*Solution.* 1. Determine the bound carbon dioxide content of the water:

$$4.70 \times 22 = 103.4 \text{ mg/litre}$$

2. Determine the sum of the free and bound carbon dioxide (*S*):

$$103.4 + 50 = 153.4 \text{ mg/litre}$$

3. Consult Table 9.1 to find the quantity 153 in column *S* and the corresponding quantity in column *G*. It is 114.7.

4. Subtract the bound carbon dioxide from 114.7:

$$x = 114.7 - 103.4 = 11.3 \text{ mg/litre}$$

Hence the test water contains 11.3 mg/litre of aggressive carbon dioxide.

**Water Saturation with Calcium Carbonate.** Stability of water is determined in practice by the index *I* of water saturation with calcium carbonate. Nomograms given in Fig. 9.7 are used for the purpose.

If the calcium ion concentration ( $\text{Ca}^{2+}$ , mg/litre), alkalinity (*A*, in mg-equiv/litre), total salt content (*P*, mg/litre) and temperature of water (*t*) are known, one can find in the nomogram the function of these arguments and determine  $\text{pH}_s$  corresponding to the equilibrium state of the system in these conditions by using the formula

$$\text{pH}_s = f_1(t) - f_2(\text{Ca}^{2+}) - f_3(A) + f_4(P)$$

Now, compare the experimental value  $\text{pH}_0$  of this water with the calculated  $\text{pH}_s$  to find the saturation index:  $I = \text{pH}_0 - \text{pH}_s$ . Water is considered to be stable if the saturation index *I* is zero. If its value is positive, the water will precipitate calcium carbonate on the

Table 9.1

Calculating Aggressive CO<sub>2</sub>

(S is the total amount of free and bound carbon dioxide, in mg/litre, G is the total amount of bound and aggressive carbon dioxide, in mg/litre)

S	G	S	G	S	G	S	G	S	G
1	1	45	43.0	89	77.3	133	104.3	177	126.2
2	2	46	43.9	90	78.0	134	104.8	178	126.6
3	3	47	44.7	91	78.7	135	105.4	179	127.0
4	4	48	45.6	92	79.3	136	105.9	180	127.5
5	5	49	46.5	93	80.0	137	106.5	181	127.9
6	6	50	47.3	94	80.8	138	106.9	182	128.4
7	7	51	48.2	95	81.4	139	107.5	183	128.8
8	8	52	49.0	96	82.1	140	108.1	184	129.2
9	9	53	49.9	97	82.7	141	108.6	185	129.7
10	10	54	50.7	98	83.3	142	109.1	186	130.2
11	11	55	51.5	99	84.0	143	109.6	187	130.6
12	12	56	52.4	100	84.6	144	110.2	188	131.0
13	13	57	53.2	101	85.3	145	110.7	189	131.4
14	13.9	58	54.0	102	85.9	146	111.2	190	131.9
15	14.9	59	54.8	103	86.5	147	111.7	191	132.3
16	15.9	60	55.7	104	87.2	148	112.2	192	132.7
17	16.9	61	56.5	105	87.6	149	112.5	193	133.2
18	17.8	62	57.2	106	88.4	150	113.2	194	133.7
19	18.8	63	58.1	107	89.1	151	113.7	195	134.0
20	19.8	64	58.8	108	89.7	152	114.2	196	134.4
21	20.8	65	59.6	109	90.4	153	114.7	197	134.8
22	21.7	66	60.4	110	90.9	154	115.3	198	135.2
23	22.7	67	61.2	111	91.6	155	115.8	199	135.7
24	23.7	68	62.0	112	92.2	156	116.3	200	136.0
25	24.6	69	62.8	113	92.8	157	116.6	210	141.6
26	25.6	70	63.5	114	93.4	158	117.3	220	145.6
27	26.5	71	64.3	115	94.0	159	117.6	230	149.8
28	27.5	72	65.0	116	94.6	160	118.1	240	153.8
29	28.4	73	65.8	117	95.1	161	118.6	250	157.5
30	29.4	74	66.5	118	95.8	162	119.1	260	161.2
31	30.3	75	67.3	119	96.3	163	119.6	270	164.9
32	31.2	76	68.0	120	97.0	164	120.1	280	168.5
33	32.2	77	68.8	121	97.6	165	120.6	290	171.9
34	33.1	78	69.5	122	98.1	166	121.0	300	175.3
35	34.0	79	70.3	123	98.6	167	121.5	310	178.8
36	34.9	80	71.0	124	99.2	168	122.0	320	182.1
37	35.9	81	71.7	125	99.8	169	122.5	330	185.0
38	36.8	82	72.4	126	100.4	170	123.0	340	188.3
39	37.7	83	73.1	127	100.9	171	123.4	350	191.3
40	38.6	84	73.8	128	101.5	172	123.9	360	194.2
41	39.5	85	74.5	129	102.1	173	124.3	370	197.3
42	40.3	86	75.2	130	102.6	174	124.7	380	199.9
43	41.2	87	75.9	131	103.2	175	125.2	390	202.8
44	42.1	88	76.5	132	103.7	176	125.7	400	205.7

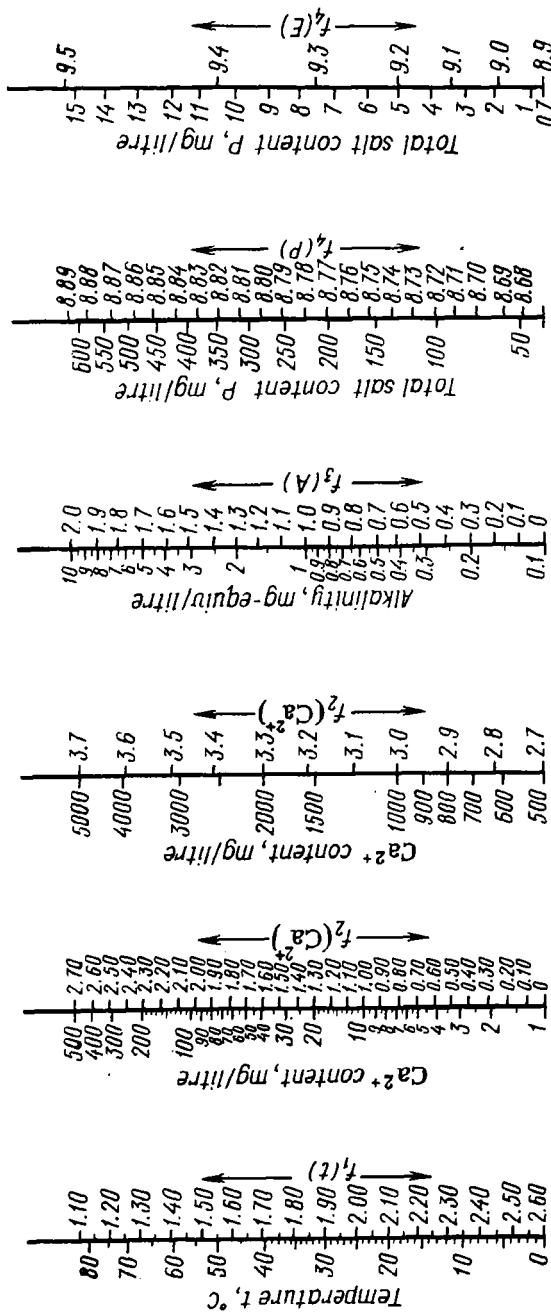


Fig. 9.7. Nomogram for determining the auxiliary values of the index characterizing the saturation of water with calcium carbonate

*apparatus walls. If the index is negative, the water is aggressive to metal and concrete. It therefore requires additional treatment (stabilization).*

**Example.** It was found that at 10°C and pH 7, a water sample contains 50 mg/litre of calcium ion, 300 mg/litre of salts, and its alkalinity is 2 mg-equiv/litre. Calculate its stability index.

**Solution.** Using the nomogram, find the functions of the given values and calculate the  $pH_s = 2.35 - 1.7 - 1.3 + 8.81 = 8.16$ . Then  $I = pH_0 - pH_s = 7.0 - 8.16 = -1.16$ . The water is aggressive, since its content of free carbon dioxide exceeds equilibrium. Hence the water should be stabilized.

## 9.5. Corrosion of Metals

*Corrosion is a spontaneous oxidative process by which metals are destroyed by chemical or electrochemical interaction of the metal with the medium.*

The essence of the chemical corrosion process is the chemical interaction of metals with the surrounding medium. Such media are known as *aggressive*. These include atmospheric air, flue gases, petrol polluted with sulphur compounds, kerosine, lubricants, impure water, etc.

Metals can be destroyed on contact with solid materials as well. For example, iron rusts on contact with chlorinated and slaked lime.

Metals can be oxidized by gases at various temperatures, but the process is most intense at high temperatures. Therefore water used for power-and-heat plants should be checked for the presence of gases whose content should be limited or, in some cases, removed.

Electrochemical corrosion involves the anode oxidation of metals. Experiments show that pure metals are stable to corrosion. They react only slightly with acids. It is explained by the fact that water molecules pass the metal ion into solution. If the metal is pure, these ions are held close to the metal by the electrons remaining in the metal. The solution in the vicinity of the metal will be charged positively. A mobile equilibrium between the metal, the ions, and the electrons in the metal is established:



The cation front holds the hydrogen cations with like charges at a certain distance from itself, precluding their contact with the metal. It is therefore difficult for the hydrogen cations to be reduced by the iron electrons. This protects pure iron from corrosion in neutral and acid media. But in practice samples of industrial iron undergo changes, because industrial iron is not uniform in composition. It contains grains of carbon (graphite), cementite ( $Fe_3C$ ), slags,

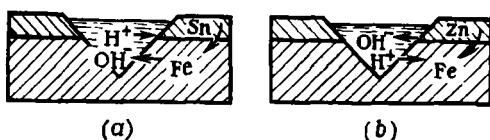
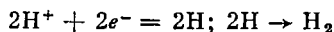


Fig. 9.8. Corrosion of iron:  
a—tin-plated; b—zinc-plated

and other foreign inclusions which do not send positive ions into solution, but which are electron conductors. The metal electrons pass over onto the inclusions to give them negative charges. The hydrogen cations do not meet any barrier of positive ions on the surfaces of the inclusions and are therefore discharged:



New ions come to replace the bound ions and a current of electrons from the metal to the inclusion is thus generated (corrosive electric current). The iron ion passes into solution. A current of positive ions arises in the liquid electrolyte. It is directed from the metal to the inclusions as well. The currents (ionic and electronic) depend on each other, they have the same level charge, but the sign of their charges is opposite.

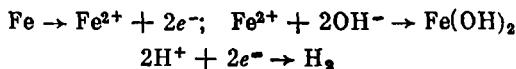
Corrosion can arise due to the nonuniform inner structure of a metal. For example, when compressed and noncompressed parts of a metal contact each other, a voltaic couple can be formed in which the compressed metal is the anode.

To prevent the corrosion of a metal, it is coated with another metal having greater stability to corrosion. But the protection is only effective if the protective coating remains intact. When the coating is mechanically damaged corrosion ruins one of the metals.

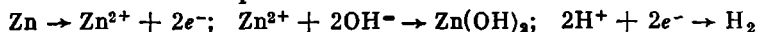
Of all metals iron is the most susceptible to corrosion. It is therefore coated with zinc, tin, nickel, etc.

When the protective coating is damaged, the corrosion process can be expressed by the following equations (Fig. 9.8):

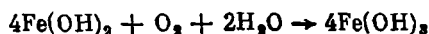
(a) corrosion of tin-plated iron:



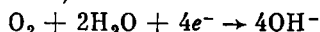
(b) corrosion of zinc-plated iron



In the former case iron rusts under the remaining intact tin coat. In the second case, however, the zinc coat is destroyed while the corrosion of iron is retarded. This is because iron is more active than tin and less active than zinc (iron comes after zinc, and tin after iron in the electromotive series of metals). Ferrous hydroxide is first formed in the corrosion process. The hydroxide is converted in moist air into ferric hydroxide:



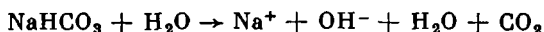
or (the electrode equation):



Corrosion of this type usually occurs in neutral waters. Oxygen is taken from water, but when it all becomes bound, it can be absorbed from the air. Corrosion through the absorption of oxygen often manifests in the form of spots with bulging of the surface over the affected sites. It can be seen on hot water mains manufactured from low-carbon steel and cast iron. To prevent corrosion, oxygen should be removed from the water before it is delivered into the boiler.

*Caustic Cracking (Caustic Embrittlement).* When low-carbon alloy steel, or stainless steel comes into contact with concentrated solutions of a strong alkali, the metal experiences the destructive process known as caustic embrittlement. The minimum concentration of alkali which causes such corrosion is from 5 to 10 per cent. Cast iron and some other metals are not affected by corrosion of this type. Caustic embrittlement induces intercrystalline corrosion.

Water used in boilers can develop high alkalinity if the starting water contains hydrocarbonates of alkaline metals which, at high temperatures, are hydrolyzed according to the equation



The high concentration of the hydroxyl ion is created because  $\text{CO}_2$  is removed from the system, and the salts are completely hydrolyzed.

One method by which the corrosion can be controlled is adding inhibitors into the water used in heat-exchange apparatus. The inhibitors retard corrosion. For example, salts of phosphoric acid form a phosphate film on metal surfaces to protect the metal from corrosion.

Rust has the following composition:  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . Rusted steel has a variable composition:  $n\text{FeO} \cdot m\text{Fe}_2\text{O}_3 \cdot p\text{H}_2\text{O}$ , where the coefficients  $n$ ,  $m$  and  $p$  depend on the corrosion conditions.

Uniform, local, and intercrystalline corrosions are distinguished (Fig. 9.9). Uniform corrosion affects the entire surface of the metal, the local form affects it only in parts, while intercrystalline corrosion occurs around separate crystals of the metal. Intercrystalline corrosion is the most dangerous of all types since it sharply decreases the mechanical strength of metal.

In order to protect metal from corrosion, it is coated with a thin film of some water-insoluble compound. Despite the thinness of the film, it protects the metal from contact with the environment, and hence from corrosion. Aluminium oxide film is an example of such a protective coating.  $\text{Al}_2\text{O}_3$  film is quickly formed on the metal surface and effectively protects it from the environment.

Iron forms a dense film on its surfaces on contact with concentrated nitric acid. The film is almost unseen to the eye but effectively pro-

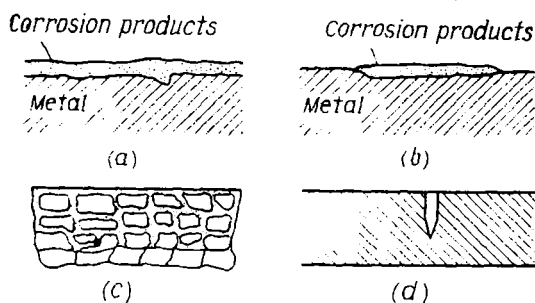


Fig. 9.9. Types of corrosion:

a—uniform; b—local; c—intercrystalline; d—corroded pit (local corrosion)

protects the metal from corrosion. But the film is brittle and cracks develop in it under friction. Protective films on iron surfaces can also be obtained by coating them with phosphates of manganese and iron. The process is known as *phosphating*.

Strong oxidizers are good corrosion-protective agents. For example, solutions of sodium chromate,  $\text{Na}_2\text{CrO}_4$ , or sodium hexametaphosphate,  $(\text{NaPO}_3)_6$ , when added to water, inhibit the corrosion of boiler material.

Hydroxyl ion contained in small quantities in water also produces a passivating action on iron. But high concentrations of alkalis in boiler water cause caustic embrittlement in the iron of boiler. A boiler is usually more strongly affected at points of rivetting because caustic alkali is accumulated in cracks and seams in a higher concentration than in water. The presence of chlorides in the water intensifies the metal decomposition since they destroy the metal protective coating.

There exists an *electrical method* of protecting steam boilers from corrosion. An anode is placed inside the boiler, while the boiler walls serve as the cathode. The current passing through this circuit acts like a voltaic couple Zn—Fe to inhibit corrosion. It also precludes the precipitation of scales on the boiler walls. The energy consumption is 2 kW·hr a day for an area of 100 sq. m.

Metal structures are protected from the aggressive action of sea water by a special method: a piece of metal (protector) is attached to the metallic structure, the electrode potential of the protector metal being lower than that of the main metal. A voltaic cell is thus formed from the protector metal and the metal of the structure, while the sea water is the electrolyte.

Triple alloys are used as protectors, for example, alloys consisting of 5-10 per cent aluminium, 5-15 per cent zinc and 75-90 per cent magnesium. The anode polarization of triple alloys is insignificant. Good results are attained with a ratio of the surfaces of the protected metal and the protector-metal of 100 : 1.

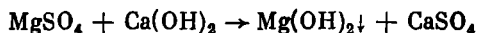
Cathodic protection does not remove the need to coat metal structures with lacquers, paints, or bitumen. Combined action is considered to be most effective against corrosion. Lacquer or paint partly insulate the metal from water to decrease the demands on the protector metal, while the protector, in turn, protects those parts of the metal structure where the paint or lacquer coating is damaged. The method is especially effective in protecting metals in contact with soil and various neutral salt solutions.

The most commonly accepted methods of fighting corrosion are coating metal articles with oil paint, enamel, or with a thin coating of another metal having greater resistance to corrosion.

## 9.6. Action of Sea Water on Concrete

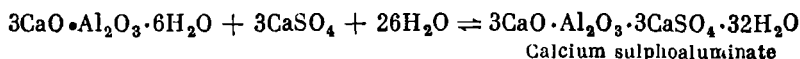
When a concrete structure is kept in the air for a long time (a few months) a protective film of  $\text{CaCO}_3$  is formed on its surfaces. The protective coating does not contain free lime and is not attacked by sea water. But if the coating is mechanically damaged, water penetrates the deeper parts of the concrete and destroys it.

The destruction of underwater structures was first noted by Michaelis and Le Chatelier in the middle of the last century. They discovered that any concrete structure is destroyed by sea water. Concrete is destroyed by water-soluble salts of sulphuric acid, for example, by magnesium sulphate contained in sea water. When the salt penetrates deep into the concrete, it reacts with lime:



All the lime of the concrete is thus gradually converted into calcium sulphate.

Moreover, calcium aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  in the concrete reacts with calcium sulphate to form calcium sulphotoaluminate:



The volume of the material expands 2.5 times. The resulting substance consists of fine needles, sometimes forming star-like formations.

Michaelis gave the name of cement bacillus to this compound because it looks like bacillus and destroys concrete.

Calcium sulphotoaluminate forms slowly in concrete. Its needle-like crystals first keep their shapes but then, under the influence of  $\text{NaCl}$ , gradually turn into a slimy mass. Gradually the connection between the cement mortar and the aggregates is weakened and the concrete breaks down. Small cracks first appear in the structure and

a white cream-like paste appears in the cracks. This is usually seen at the boundary between the liquid and the gas phases, at the surface of water. The destruction gradually propagates to all parts of the structure which is thus ruined.

Concrete can also be affected by fresh water, by water containing carbon dioxide, and by mineral waters.

The stability of concrete structures greatly depends on the presence in water of hydrocarbonates, because an equilibrium is established between the carbonate film of concrete  $\text{CaCO}_3$  and hydrocarbonate  $\text{Ca}(\text{HCO}_3)_2$  of the water. This equilibrium protects the film from dissolution. The absence from the water of hydrocarbonates weakens the binding properties of cement, and the mortar softens due to leaching of the calcium ion.

To control the destructive effect of water passing through silicate cements and concretes, the use of fatty compositions which are less penetrable to water is recommended. Special water-repelling substances, such as ceresits, cerolits, hydrosit, etc., are added to mortars or cements to give concrete greater resistance, or concrete structures are coated on the outside with a water-repelling material, such as resin, goudron, or else concrete is gunited.

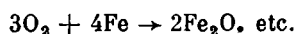
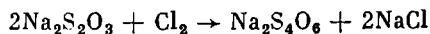
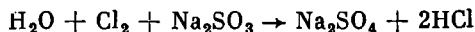
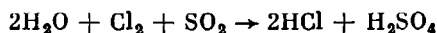
Concrete pipes are often wrapped in tar asphalt-impregnated paper to protect them from carbon-dioxide waters. It is important that the concrete in the irrigation structures should be dense and the surfaces be well covered with water-repelling compounds.

## 9.7. Removal of Gas from Water

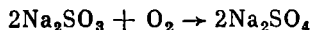
Dissolved gases, such as  $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , etc., are removed from water by various chemical, physical, and physico-chemical methods.

The *chemical treatment* of water involves adding special substances to the water which quantitatively react with the dissolved gases. For example,  $\text{SO}_2$ , sodium thiosulphate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , sodium sulphite  $\text{Na}_2\text{SO}_3$ , ferrous sulphate  $\text{FeSO}_4$ , ammonia  $\text{NH}_3$ , and other substances are used to remove chlorine (dechlorination). Oxygen is removed from water by iron chips, sulphites,  $\text{SO}_2$ , etc. Carbon dioxide is bound with  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaO}$ ,  $\text{CaCO}_3$ .

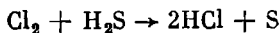
The reactions are as follows:



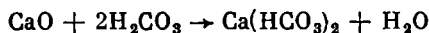
The last reaction is especially energetic at high temperatures. At 25°C, it continues for 25-30 minutes, while at 80°C it is completed in 3 minutes:



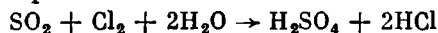
Hydrogen sulphide can be bound with chlorine with subsequent coagulation of sulphur:



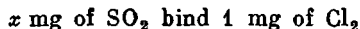
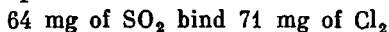
Carbon dioxide, as carbonic acid, reacts with the chemical agents according to these equations:



Any substance that reacts with gases can be used to remove them from water. The only requirements are the harmlessness of the substances themselves and of the products of their combination with the gases, and cheapness. The dose of the chemical should be determined empirically by trial treatment of water samples, or by stoichiometric calculations, provided the concentration of the gas contained in the water is known. For example, sulphur dioxide reacts with chlorine according to the equation



The following proportion can be set out:



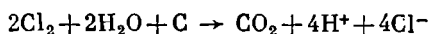
Whence

$$x = \frac{64 \times 1}{71} = 0.9 \text{ mg of SO}_2$$

The chemical method of removing gas from water requires strict control since overdosage will impair the quality of the water. Physical and physico-chemical methods are simpler and lessen the danger of water pollution with new reaction products.

*Mutation filtration is physico-chemical method* of water treatment. Water is passed through a bed of a filtering agent capable of reacting chemically with the contaminants contained in the water, the products of the reaction being carried away with the water. Mutation filtration thus involves the consumption of the filtering material.

Common nonactivated charcoal is used in mutation filters to remove chlorine from water. The reaction which occurs in the filter can be expressed like this:



The filtering material is oxidized and the reaction products are carried away with the water. The rate of these reactions is relatively slow. When water rich in chlorine passes the first layers of the filter, only a small portion of chlorine is bound. When the water comes in contact with the next portion of the filter material, its chlorine content is lower, and it becomes even lower when the water passes to next portions of the filter material. Hence each new layer of the filter comes in contact with water whose chlorine content is becoming successively lower.

The height of the mutation filter bed can be calculated tentatively by the following formula

$$H = K \sqrt{v} \log \frac{c}{c-x}$$

where  $H$  is the height of the filter bed, in cm;  $v$  is the volume of water, in ml, which passes through a square centimeter of the filter section in one minute (the filtration rate, in cm/min);  $c$  is the initial concentration of solute, mg/litre;  $(c - x)$  is the concentration of the solute at a given height of the filter, mg/litre; and  $K$  is the proportionality coefficient.

**Example.** It is necessary to treat water containing 2 mg/litre of chlorine using a carbon filter. It has been established in preliminary tests that with the given particle size of the coal charge and a filtration rate of 500 ml per sq. cm. per minute,  $K = 0.60$ . Dechlorination should decrease the chlorine concentration to 0.01 mg/litre. Calculate the required height of the filter for a filtration rate of 2 litre/minute per sq. cm of the filter section

*Solution.*

$$H = 0.6 \sqrt{2000} \log \frac{2}{0.01} = 62 \text{ cm}$$

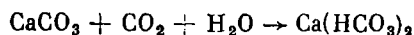
In practice the filter bed is 2-3 times higher. In our case it is 1.5-2.0 meter high.

When water containing chlorine is treated on a carbon filter, HCl and colloids are adsorbed on coal particles to form a film on them which interferes with the contact of chlorine with the coal and the filter becomes gradually exhausted. To restore the filtering power of coal it is washed with pure water, a hypochlorite solution, alkali, calcium chloride solution, and with pure water again. The adsorbed substances are peptized to recover the filtering surfaces.

Activated carbon should not be used in mutation filters, since adsorption interferes with the main reaction.

Aggressive carbon dioxide is removed by passing water through a mutation filter packed with crushed marble. The reaction is as

follows



*Physical methods* are based on the Henry-Dalton law: (1) the solubility of gases decreases with the partial pressure over the solution; (2) the solubility of gases decreases with rising temperature.

The period of the liberation of a gas from water into the air can be calculated using the formula suggested by Bohr:

$$\tau = \frac{v (\log c_0 - \log c)}{S \beta \log e}$$

where  $\tau$  is the time during which gas passes from water into the air, in minutes;  $v$  is the volume of water, cu.m;  $S$  is the surface area of contact between the liquid and the gas phases, sq.m;  $c_0$  is the initial concentration of gas in water at 0°C and 760 mm Hg, g/cu.m;  $c$  is the final concentration of gas in water at the moment of time  $\tau$  under the same conditions, g/cu.m;  $e$  is the base of the natural logarithm;  $\beta$  is the desorption coefficient\*, which depends on the stirring intensity, temperature and nature of dissolved gas. The value of  $\beta$  increases with intensity of stirring and with temperature.

The concentration of dissolved gas affects the value of  $\beta$  only during chemical interaction of the dissolved gas with water: at 20°C  $\beta$  is about 1 for  $\text{H}_2$ ,  $\text{O}_2$ , and other sparingly soluble gases;  $\beta$  is 0.07 for  $\text{H}_2\text{S}$ ; 0.015 for  $\text{NH}_3$  and 0.153 for  $\text{CO}_2$ .

The time during which gases are displaced from water is determined mainly by the ratio  $v/s$ . To accelerate the process, the interface between the liquid and the gas phase ( $S$ ) should be increased,  $v$  remaining constant. To attain this, water is sprayed, sprinkled, passed through cooling towers, sprayed in vacuum, or air is bubbled through water.

The apparatus used for the purpose are perforated tanks, from which water issues in thin jets, or sprinklers installed in water pipes at a height of 1.2-1.5 m from which water falls in little fountains into concrete receptacles.

When water is treated in cooling towers, it falls onto coke or is sprinkled over lattices.

The partial pressure of the unwanted gases in the air over the liquid is lowered by intense ventilation in the enclosure where the water is sprinkled.

The removal of gas from water is especially effective in a vacuum in boilers of special design with simultaneous heating of the water.

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\* The desorption coefficient is the rate of displacement from the liquid of gases and substances in the vapour state absorbed in the liquid.

## 9.8. Removal of Smack and Odour from Water (Deodoration)

*The deodoration of water is the process by which foul or unpleasant odours and smacks given to water by various impurities which are often present in water in quantities that cannot be determined analytically are removed.*

Odour can be due to phenols, hydrogen sulphide, chlorine, soluble salts, etc. Unpleasant odour and smack can also be due to synthetic surface active substances. Pesticides, i.e. chemical poisons used in agriculture to control insects, often enter water bodies in rain runoff and melting snow. They give the water unpleasant odour and smacks even when in negligible quantities. For example, thiophos can be smelt in as small a concentration as 0.2 mg/litre, and DDT at 0.07 mg/litre.

The method most commonly used to remove odour is passing water through activated coal which adsorbs the contaminants.

Phenols and chlorophenols are destroyed by *pre-chlorination* of water. This gives polychloro-derivatives devoid of unpleasant odour (the dose of chlorine is sometimes as high as 10-12 mg/litre, hence the need for subsequent dechlorination).

The deodorizing effect of chlorine can be strengthened by adding permanganate. It can be added to the water before or after chlorination; sometimes it is used for independent oxidation in the absence of chlorine. If  $\text{KMnO}_4$  is added before chlorination, it destroys organic substances having unpleasant odour and taste, and if added after chlorination, it destroys the chlorine derivatives formed during chlorination. The dose of potassium permanganate is normally from 0.1 to 0.25 mg/litre.

To improve the taste of water containing phenols, *pre-ammoniation* is used. The oxidation potential of the chloramine thus formed (0.76 V) is lower than that of chlorine (1.36 V). The chloramine does not therefore react with phenols and does not form unpleasant chlorophenolic odour and taste in water.

Pre-ammoniation precludes the odour of residual chlorine, and decreases the probability of the subsequent development of bacteria and pipe rusting. But pre-ammoniation does not destroy odours and smacks due to microorganisms. The process involves treating water with ammonium sulphate or ammonia. The weight ratio of ammonia to chlorine should be 1 : 1 or 1 : 2.

Powdered carbon (coal suspension) is sometimes added to water in order to remove odour. Carbon treatment should be applied to water before coagulation, after coagulation, or simultaneously with it. According to the literature, the amount of coal used varies from

0.5 to 15 mg/litre. It is very important that the pore size should correspond to the size of the adsorbed molecules. This method can be used to remove dyes contained in water.

Ozonization is another method used to improve the taste of water. It is used to separate water from synthetic surface active substances, but it is ineffective against pesticides which are stable to strong oxidants. The concentration of these pollutants is decreased in water by coagulation with aluminium or iron coagulants.

Mineral substances are removed from water by alkalyzing with lime or by filtration through roasted dolomite. This method is used to remove lead, copper, zinc, titanium, vanadium, tungsten, molybdenum, uranium, nickel, cobalt, and mercury. Arsenic in inorganic compound form is removed from water by chlorination and coagulation with iron-containing coagulants in an alkaline medium, and by aeration. Boron contained in water as  $\text{BO}_3^{3-}$  (or  $\text{BO}_2^-$ ) can be removed in an anion-exchanger with subsequent recovery of the filter with sulphuric acid. Phosphates are removed from water by activated alumina (20 kg of  $\text{PO}_4^{3-}$  per ton of sorbent). They are also removed by lime during water softening (up to 1-2 mg/litre of residual  $\text{P}_2\text{O}_5$ ). Ammonium salts are removed from water by cation exchangers,  $\text{NaR}$ ,  $\text{CaR}_2$ , or  $\text{HR}$ . Moreover, if the ammonium ion is present in large quantities, it is removed from water as  $\text{NH}_3$  by vacuum treatment in an alkaline medium.

A prophylactic measure to prevent unpleasant odours and smacks in water is the cleaning of decaying vegetation from the bed and banks of rivers and of other water bodies, and also the cleaning and disinfection of the water treatment units.

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## 9.9. Softening and Desalting of Water

**Hardness of water.** Natural water containing large quantities of dissolved salts of calcium and magnesium is called *hard*. The salts responsible for hardness are not harmful to man, but when magnesium is contained in large quantities it impairs the organoleptic properties of water. The maximum allowed quantity of magnesium oxide in water is 15 mg/litre. Excess magnesium salts (over 50 per cent of the total volume of liquid) makes water softening a difficult problem.

Total, temporary, permanent, carbonate and noncarbonate hardnesses are distinguished.

*Total hardness* is the total concentration of the ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$  in water, expressed in mg-equiv/litre.

*Permanent hardness* is that part of the total hardness which remains in water after boiling under atmospheric pressure for a specific period of time.

*Temporary hardness* is that part of the total hardness which can be removed by boiling water under atmospheric pressure for a specific period of time. It represents the difference between total and permanent hardness.

*Carbonate hardness* is the part of total hardness equivalent to the concentration of carbonates and hydrocarbonates of calcium and magnesium.

*Noncarbonate hardness* is the part of total hardness equal to the difference between total and carbonate hardness.

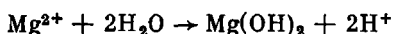
Using hard waters for domestic and industrial purposes is undesirable for the following reasons:

1. A lot of soap is required for washing. The ions of calcium and magnesium react with soaps, which are salts of fatty acids, to give insoluble precipitates  $(C_{15}H_{31}COO)_2Ca$  and  $(C_{17}H_{35}COO)_2Ca$ , and similar salts of magnesium. Water with a hardness of 7.1 mg-equiv will require the use of an extra 2.4 g per litre of soap.

2. The premature wearing out of fabrics after laundering in hard waters. The fibres adsorb calcium and magnesium salts and this makes them brittle.

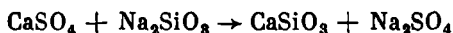
3. Meat and beans lose much of their nutritional goodness when boiled in hard water; the boiling time is increased, and proteins extracted from meat pass into an insoluble form and their assimilation becomes difficult.

4. The intense corrosion of boilers and heat-exchangers due to the hydrolysis of magnesium salts and the increased concentration of the hydrogen ion in solution:



5. Scale deposits on the surfaces of heat exchangers (boilers, condensers) reduce the efficiency of such equipment. Scale has low heat conductivity and increases fuel consumption. Metal under scale deposits overheats and becomes soft. Boiler tubes begin to bulge and crack. The scale should therefore be removed periodically.

Scaling is connected with the thermic decomposition of hydrocarbonates, hydrolysis of carbonates, and also decreased solubility in hot water of calcium sulphate, magnesium hydroxide, and silicates of calcium and magnesium. The concentration of these substances increases in boilers during water evaporation. Moreover, additional quantities of silicates of magnesium and calcium can be formed at high temperatures:

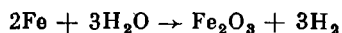


Salts of iron, manganese, aluminium, and suspended and colloidal particles are also involved in the formation of scale. The scale deposit can sometimes be so thick that it almost totally blocks the passage.

Boiler scale can be classified thus:

1. *Sulphate scale*, containing up to 95 per cent of  $\text{CaSO}_4$ , having relatively high heat conductivity.
2. *Carbonate scale* containing up to 90-95 per cent of  $\text{CaCO}_3$ , having lower heat conductivity than sulphate scale.
3. *Silicate scale* containing up to 45-48 per cent of  $\text{SiO}_2$ , having low heat conductivity.

Metal under scale is destroyed by the following process. When a layer of scale dries up, it cracks and steam enters the cracks to react with the boiler metal:



Fistulas are thus formed in the walls. The liberated hydrogen reduces sulphates to  $\text{H}_2\text{S}$ , which reacts with the boiler metal to intensify the corrosion.

**Units of Hardness.** There is no universal unit for the hardness of water, and various units are used in different countries.

German degrees:  $1^\circ = 1$  mg of  $\text{CaO}$  in 100 ml of water or 1 g in 100 litres of water.

French degrees:  $1^\circ = 1$  g of  $\text{CaCO}_3$  in 100 litres of water.

British degrees:  $1^\circ = 1$  g of  $\text{CaCO}_3$  in 70 litres of water.

American degrees:  $1^\circ = 1$  g of  $\text{CaCO}_3$  in 1000 litres of water.

Since 1951, a new unit has been used in the Soviet Union to express the hardness of water, expressed in milligram-equivalents per litre of water. According to GOST 6055-61, 1 mg-equiv of hardness corresponds to 20.04 mg/litre of  $\text{Ca}^{2+}$  or 12.16 mg/litre of  $\text{Mg}^{2+}$ .

To measure low levels of hardness, a microgram-equivalent is used, this being 0.001 of a mg-equiv.

*Hardness units relate as follows*

	mg-equiv/ litre	German degree	French degree	British degree	American degree
1 mg-equiv/litre . . . . .	1	2.804	5.005	3.511	50.045
1 German degree . . . . .	0.35663	1	1.7848	1.2521	17.847
1 French degree . . . . .	0.19982	0.5603	1	0.7015	10
1 British degree . . . . .	0.28483	0.7987	1.4255	1	14.253
1 American degree . . . . .	0.01998	0.0560	0.1	0.0702	1

According to hardness, all waters are classified as follows: (1) very soft (hardness from 0 to  $4^\circ$ , or from 0 to 1.5 mg-equiv/litre); (2) soft (hardness from  $4^\circ$  to  $8^\circ$ , or from 1.5 to 3 mg-equiv/litre); (3) medium hard (from  $8^\circ$  to  $12^\circ$ , or from 3 to 4.5 mg-equiv/litre); (4) moderately hard (from  $12^\circ$  to  $18^\circ$ , or from 4.5 to 6.0 mg-equiv/litre); (5) hard (from  $18^\circ$  to  $30^\circ$  or from 6 to 10 mg-equiv/litre); (6) very hard (over  $30^\circ$ , or over 10 mg-equiv/litre).

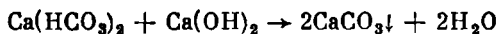
**Chemical Softening of Water.** *The process by which water hardness is decreased is called softening.* It involves decreasing the concentration of calcium and magnesium salts in water.

Water used to feed boilers is usually softened. Residual hardness of water can vary depending on the type of boiler and the working pressure in it.

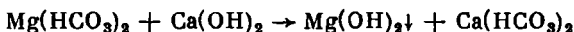
The existing methods of softening water can be divided into the following three groups: adding chemical reagents, ion-exchange processes, and thermic softening.

The three methods are often used in various combinations: reagents are added to water treated in ion-exchangers and to thermally treated water.

*Soda-lime Softening.* When slaked lime,  $\text{Ca}(\text{OH})_2$ , is added to water, calcium salts are precipitated as  $\text{CaCO}_3$ :

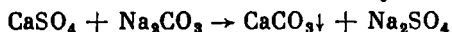


while magnesium hydrocarbonate reacts with lime to precipitate as magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ :



the  $\text{Ca}(\text{HCO}_3)_2$  thus formed reacts with lime according to the given equation.

Noncarbonate hardness can be removed by adding soda:



The precipitate is formed in two steps: first  $\text{CaCO}_3$  is formed and its crystals then grow. Fine precipitate is difficult to settle and its particles should therefore be enlarged. The slow crystallization process can be accelerated by heating or by adding centres of crystallization ( $\text{CaCO}_3$  suspension) into water. The heating however makes the process more expensive, and it is only justified when water would have to be heated anyway. The method is not applicable to waters containing large amounts of finely dispersed organic matter (about 100 mg/litre and over), since this matter will stabilize the calcium carbonate and thus interfere with the growth of its crystals.

In such cases water should be softened after coagulation, or simultaneously with it. Combined coagulation and softening is effected in two stages:

(1) a coagulant and a part of the lime are first added to ensure the optimum coagulation conditions;

(2) soda and the rest of the lime are added to soften the water.

The lime and soda doses are determined experimentally. The following empirical formulas can be used for tentative calculations:

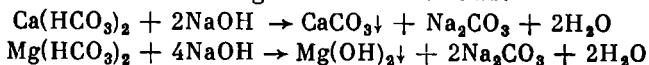
$$D_{\text{CaO}} = ([H_c] + [\text{Mg}^{2+}] + [\text{CO}_2] + 0.5) 28$$

$$D_{\text{Na}_2\text{CO}_3} = ([H_{\text{noncarb}}] + 0.5) 53$$

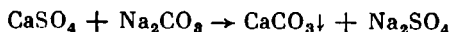
where  $D_{\text{CaO}}$  is the dose of calcium oxide, mg/litre;  $D_{\text{Na}_2\text{CO}_3}$  is the dose of soda, mg/litre;  $[H_c]$  is the carbonate hardness, mg-equiv/litre;  $[\text{Mg}^{2+}]$  is the magnesium hardness, mg-equiv/litre;  $[\text{CO}_2]$  is the carbon dioxide level, mg-equiv/litre;  $[H_{\text{noncarb}}]$  is the noncarbonate

hardness, mg-equiv/litre; 0.5 is the excess reagent, mg-equiv/litre; 28 is the equivalent weight of calcium; and 53 is the equivalent weight of soda.

*Softening Water with Sodium Hydroxide.* Sodium hydroxide binds cations of calcium and magnesium as follows:



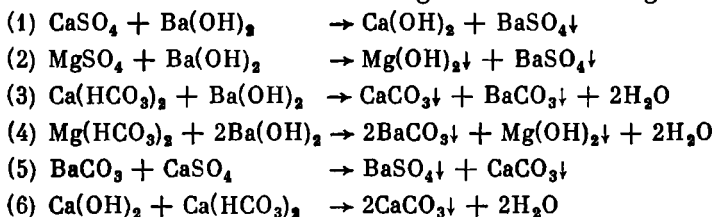
The soda thus formed reacts with noncarbonate hardness to partly remove it from water



It follows that sodium hydroxide removes the carbonate hardness and the part of the noncarbonate hardness equivalent to the amount of sodium carbonate formed.

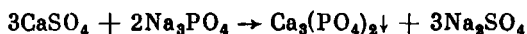
*Softening Water with Barium Salts.* This method is similar to that in which soda and lime are used, but it has the advantage that the salts formed are insoluble in water. The level of the salts responsible for the hardness decreases and the softening is more complete. Since  $\text{BaCO}_3$  is insoluble, the dosage of the reagents does not require accuracy and the process can proceed on its own.

The reactions which occur during barium softening are as follows:



Barium salts stimulate the complete removal of salts from water rather than the replacement of one salt for another. This is the main advantage of the method. The disadvantage is the high cost of barium salts and low reaction rates with barium carbonate,  $\text{BaCO}_3$ .

*Softening Water with Phosphates.* Trisodium phosphate used in this process forms sparingly soluble salts of calcium and magnesium:



This method is used for complete softening of water after the main hardness has already been removed, for example, by the soda-lime method (to residual hardness of 0.35-0.7 mg-equiv/litre).

Trisodium phosphate gives good results but the salts of phosphoric acid are expensive and they are only used when water of very high softness is required.

Salts of phosphoric acids are used to treat water inside the boiler. *Descaling agents* are added for the purpose. These agents must possess high descaling properties; they should be free from any substances

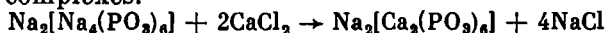
that could be harmful to the personnel, and be readily available, and easy to batch.

*Antidepon* is one of such descaling agents. It consists of 60-80 per cent of  $\text{Na}_3\text{PO}_4$  and 40-20 per cent of organic substances such as starch, cork meal, and tanning substances. The descale components are centres of crystallization for salts of calcium and magnesium, and instead of depositing on the boiler walls, these salts deposit in the bulk of the water. When *Antidepon* is added to the water, crystals are formed of difficulty soluble phosphates of calcium and magnesium, around which crystallize the substances, which otherwise deposit on the boiler walls. The precipitated substances are periodically removed from the boiler as *sludge*. The organic component of the descaling agent prevents the formed crystals from baking by stabilizing fine crystals.

Trisodium phosphate in combination with colloidal graphite and ferric tannate is an especially effective descaling agent. It effectively softens water and stimulates the formation on the boiler walls of an iron phosphate film which is strong and highly resistant to corrosion. The descaling agent can also soften old dense scale in the boiler.

Colloidal graphite (particles sizing from 0.1 to 10 millimicrons) suspended in water is also useful to fight scaling: it forms a precipitate which can easily be removed by rinsing.

To soften water at temperatures below  $70^\circ\text{C}$ , sodium hexametaphosphate is recommended. It binds the calcium and magnesium ions into complexes:



To bind 1 mg-equiv of scaling substances, 0.42 g of  $(\text{NaPO}_3)_6$  is required.

At temperatures over  $70^\circ\text{C}$ , sodium hexametaphosphate converts into the orthophosphate whose softening properties are worse than of the metaphosphate.

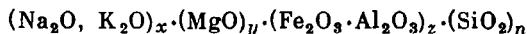
Magnetic treatment of water also reduces scale formation: the crystals of scaling substances are precipitated inside the bulk of the water rather than on the boiler walls.

**Ion-Exchange Softening.** *Substances capable of sorption exchange of ions with the electrolyte solution are called ion-exchangers.* Ion-exchangers are porous solids swelling in water without dissolving in it. According to the composition of the main skeleton which binds the ionogenic groups into a whole, the ion-exchange materials are classified as (1) mineral and (2) organic. The former are numerous silicates, aluminosilicates, aluminium hydroxide, zirconium phosphate, and the like materials. The latter are the products of chemical treatment of coal or lignin, or man-made high-molecular organic compounds containing the ionogenic groups.

Natural or artificial ion-exchangers can be used for water treatment. Natural materials are glauconites and humic coals. Man-made

ion-exchange materials are sulphonated coals and synthetic ion-exchange resins.

*Glaucanites* are amorphous ferroaluminosilicates, whose composition can tentatively be described by this formula:



Glaucanite sand is first separated from extraneous matter (clay and quartz), treated at a temperature of 300-400°C to give it sufficient strength and water resistance, and then treated on a magnetic separator to remove residual rock.

The glaucanite prepared consists of fine smooth green grains sizing 0.2-0.6 mm, having the density of 2.20 to 2.85 g/cc. Glaucanite can be used in neutral and alkaline media, since the grains partly dissolve in an acid medium.

*Humic coals* are used to prepare cation-exchangers. They should contain not less than 15 per cent of humic acids. Crushed to 0.75-1.0 mm grains, humic coals are passed through a sieve to separate from dust and undersized particles, and treated with a 15 per cent solution of sodium chloride, acidified with HCl to pH 2.0, for 2-3 hours.

Natural ion-exchangers are inferior to synthetic ion-exchange resins and the latter are therefore mostly used.

*Sulphonated coals* are prepared by treating coals extracted at the Donetsk and Kuznetsk coal basins with concentrated sulphuric acid. To that end, coal is crushed to 1-5 mm particles and mixed with oleum ( $\text{H}_2\text{SO}_4$  containing 18-20 per cent of  $\text{SO}_3$ ) or oil of vitriol (96 per cent sulphuric acid) in the ratio of 1 : 4. Sulphonation is carried out at a temperature of 180-200°C for six hours. The coal is then washed to remove excess acid and separated into fractions by the size of particles.

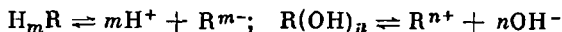
*Ion-exchange resins* are three-dimensional network polymers, insoluble in water but swelling in it to a limited extent, and containing ionogenic groups, i.e. groups capable of ion-exchange. The number and the length of bridges cross-linking the linear polymer chains determine the fineness of the cells, which is very important for the properties of the ion exchangers.

For example, if the cells are large, the resins can swell to a greater extent and the diffusion rate will be greater than with fine cell resin.

*Cation- and anion-exchangers* are distinguished. Substances that exchange cations are called cation-exchangers and those exchanging anions, are called anion-exchangers.

Cation exchangers dissociate into small mobile cations capable of exchange (e.g.  $\text{H}^+$ ) and high-molecular anions ( $\text{R}^{m-1}$ ), while anion-exchangers fall into small easily moving anions (e.g.  $\text{OH}^-$ ) and a high-molecular cation ( $\text{R}^{n+}$ ).

The dissociation can be described, conventionally, like this:



where  $m$  and  $n$  are the quantities of mobile ions in cation- and anion-exchangers.

Most common cation-exchange resins are produced by polycondensation of phenols and formaldehyde, and also polymers, the products of copolymerization of styrene and diene hydrocarbons.

The most popular anion-exchange resins are aminoformaldehyde and polystyrene anion-exchangers, the addition products of the main groups to copolymers of styrene.

All ion-exchangers can have similar or different ionogenic groups. Cation-exchangers with mixed functional groups occur in the following combinations: (1) sulpho-acid and hydroxyphenolic; (2) sulpho-acid and carboxylic; (3) residues of phosphoric acid and hydroxyphenolic; (4) arsenic and hydroxyphenolic; (5) carboxylic and hydroxyphenolic.

There are the following anion-exchange resins with similar ionogenic groups: (1) quaternary ammonium bases; (2) tertiary amines; (3) secondary amines; (4) primary amines, (5) quaternary sulphonium bases\*.

Anion-exchange resins with different ionogenic groups comprise amino variously substituted groups.

By the degree of dissociation ion-exchangers are classified as (1) strongly acid, (2) weakly acid, (3) strongly basic, and (4) weakly basic.

Strongly acid cation-exchangers exchange ions with the dissolved salts in a neutral and acid medium (sulpho- and phosphate cation exchangers). Weakly acid cation-exchangers, containing carboxylic or hydroxyphenolic groups, exchange their proton for cations of salts of weak acids in neutral solution, the rate of exchange increasing with pH of the medium.

Strong anion-exchangers react with salt solutions in neutral and even weakly alkaline media. Weakly basic anion-exchangers exchange their ions only in acid media, the completeness of the exchange of the hydroxyl group for the anion of the dissolved electrolyte growing with acidity of the medium.

The ionogenic groups in strong electrolytes are quaternary ammonium or sulphonium bases, while in weakly basic electrolytes these are primary, secondary and tertiary amines.

The strength of the ionogenic groups greatly depends on the other functional groups connected directly with them. For example, the

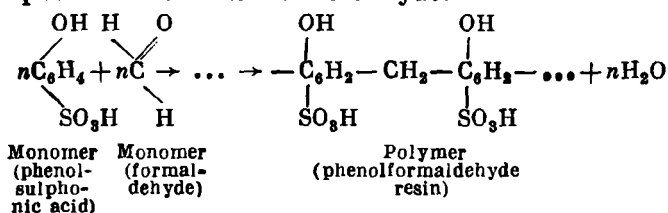
\* Sulphonium bases are coordination compounds, derivatives of thioethers, e.g.  $2C_2H_5I + K_2S \rightarrow (C_2H_5)_2S + 2KI$ . Sulphur adds alkyl halides, salts, etc.,  $(C_2H_5)_2S + CH_3I \rightarrow [(C_2H_5)_2S(CH_3)]I$ . By analogy with ammonium compounds, these addition products are called sulphonium salts, while  $[(C_nH_{2n+1})_3S]OH$ , sulphonium bases, the compounds similar to alkalis by their basicity.

benzene ring decreases the dissociation degree of amines. The carbonyl group produces the same effect on the dissociation of the neighbouring amino group. The presence of two or three hydroxyl groups at one benzene ring markedly increases the ionization of the ion-exchanger.

Hence most *cation-exchangers* are polymeric polyfunctional acids comprising the groups  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{OH}$ ,  $-\text{SH}$ ,  $\text{SiOOH}$ , and others.

*Anion-exchangers* are high-molecular compounds comprising a great number of basic groups such as  $-\text{NH}_2$ ,  $-\text{NH}_3\text{OH}$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ , etc. One ion-exchanger can contain ionogenic groups of various acidity and basicity.

The ionogenic groups are introduced into the ion-exchanger together with the monomer, as is the case with copolycondensation of phenolsulphonic acid with formaldehyde:



or by chemical treatment of the polymer (sulphonation of the styrene copolymer with divinylbenzene, or nitration of the same copolymer with subsequent reduction of the groups  $-\text{NO}_2$  to  $-\text{NH}_2$ ). The selection of a particular ionogenic group depends on the purpose of the given ion-exchanger.

Spherical grains are normally used for water filtration. These are prepared by suspension polymerization or mixing of molten, "non-cross-linked" resin in an inert solvent with subsequent cooling. Loose ion exchangers provide good conditions for the movement of the liquid through it.

The mobility of the ions  $\text{H}^+$  and  $\text{OH}^-$  in the resin depends on the character of the ionogenic groups. The hydrogen ion moves freely in the resin phase of a strong cation exchanger comprising for example, the sulpho group  $-\text{SO}_3\text{H}$ . The hydrogen ions freely change places without violating the electric neutrality. The high-molecular part of polyelectrolyte, which is a gigantic cation or anion, is completely immobile.

When the ion-exchanger particles are immersed in water, they swell\* and their spatial molecular network expands (Figs. 9.10 and 9.11).

\* The swelling is due to the tendency of particles to hydration and electrostatic repulsion of fixed ions with like charges. Swelling is continued until an equilibrium is attained between the osmotic pressure in the system and the opposing elastic force of the flexible hydrocarbon chains.

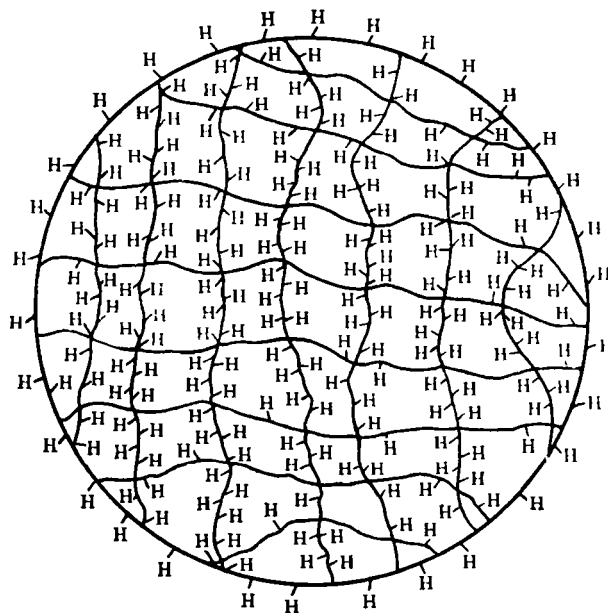


Fig. 9.10. Structural distribution of exchangeable ions in a swollen grain of cation-exchanger

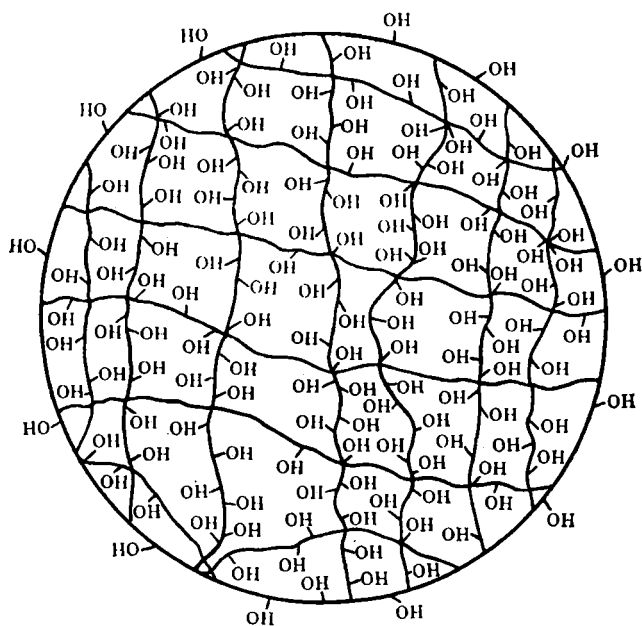


Fig. 9.11. Structural distribution of exchangeable ions in a swollen grain of anion-exchanger

The swollen ion-exchanger is a solution of electrolyte and has the general properties of such a solution. It differs from normal electrolyte by the limited mobility of the ions. The mobile ions connected with the polymer structure by the action of the polar molecules of water pass into liquid leaving the oppositely charged particle of the ion-exchanger, but their mobility in the solution is limited by the electrostatic attraction of this particle. Hence an electrical double layer arises around the polymer granule. But if other ions with like charges occur in the vicinity of mobile ions, they take the place of the mobile ion, while the mobile ions are freed from the electrostatic effect of the ion-exchanger and pass into solution. The ion-exchange process is thus effected.

The exchange process is underlied by a chemical reaction occurring in the outer and the inner surfaces of the ion-exchanger. The ion-exchange occurs within the range of strictly limited equivalent quantities.

The exchange reactions in solution occur practically instantaneously, but the rate of ion-exchange processes occurring in a heterogeneous medium can be measured. The rate of the process, which can practically be assessed, depends on the rate of diffusion which is the slowest stage of the ion-exchange process. This is confirmed by the drop in the overall rate of the ion-exchange process with increasing size of the ion-exchange grains.

The ion exchange in solutions is a selective process. As the absolute concentration of the solution decreases, polyvalent ions are adsorbed better than monovalent ones, while at high concentrations, the monovalent ion is adsorbed. For example, when water is softened (dilute solution), the ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are adsorbed selectively, while the  $\text{Na}^+$  ion is not practically adsorbed. When treated with a concentrated solution of  $\text{NaCl}$ , the divalent metal ions are displaced from the cation-exchanger by the sodium ion. This is used to recover cation-exchangers.

The main property which is important in ion-exchangers is their *exchange capacity*. It depends on the quantity of the ions extracted from water by one gram of air-dry ion-exchanger.

An ionic atmosphere of mobile ions is formed as a result of dissociation occurring around the solid phase of the ion-exchanger. Ionic atmosphere is found inside a very limited space in the solvent. The activity of an ion-exchanger and its working capacity increase with the dimensions of the ionic atmosphere formed around the grains.

The capacity of an ion-exchanger depends on the number of sites available for the exchange which in turn depends on the ion dimen-

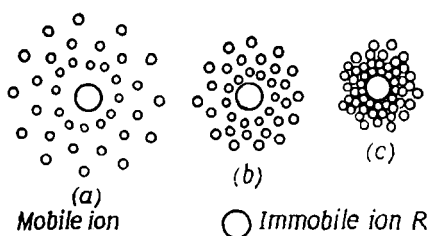


Fig. 9.12. The effect of acid concentration on the ionic atmosphere:

a—in distillate; b—in an acid solution of low concentration; c—in an acid solution of high concentration

sions. The ionization degree at a given pH, the nature, and the concentration of the ion in solution are also important.

The effect that the pH of the medium has on the exchange capacity of all materials is great. When pH increases, the exchange capacity of cation-exchangers increases and of anion-exchangers decreases, and vice versa. The exchange capacity of sulphonated cation-

exchangers containing only one type of active particles,  $-\text{SO}_3\text{H}$ , does not practically depend on the pH of the medium because this cation-exchanger is a strong electrolyte and the hydrogen ion concentration does not affect its dissociation. The dependence of the exchange capacity on the pH is marked in polyfunctional cation-exchangers\* containing weak acid groups  $-\text{COOH}$  and  $-\text{OH}$  along with strong acid groups  $-\text{SO}_3\text{H}$ . In this case, at low pH, the dissociation of weak acids will be significantly inhibited by the increased concentration of the hydrogen ion (Fig. 9.12c). The ionic atmosphere will be "pressed" to the nucleus to decrease the exchange capacity. This will not occur if the pH of the water is above 7.

H- and Na-cation-exchangers are commonly used in water purification. Depending on the cation, H- and Na-cation-exchange processes are distinguished. When water is treated on an H-cation-exchanger, its acidity increases, and when treated on a Na-cation-exchanger the alkalinity of water grows provided the initial water contains carbonate hardness.

Hence, not only sulfo-groups,  $-\text{SO}_3\text{H}$ , but also the carboxyl and hydroxyl groups,  $-\text{COOH}$  and  $-\text{OH}$  respectively, take part in exchange reactions with the Na-cation exchangers, provided they are present in them. Meanwhile, sulfo-groups exchange their ions mainly with H-cation-exchangers. Therefore, the effect of softening water with noncarbonate hardness on the H-form polyfunctional cation-exchangers will be low due to the "compression" of the ionic atmosphere.

Thus, the exchange capacity will be higher with higher dissociation of the active groups of the ion-exchanger, and with a greater number of the active groups per ion-exchange micelle.

\* Polyfunctional cation-exchangers are those containing various active groups, such as  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{SO}_3\text{H}$ .

The exchange capacity of various materials differs greatly, and is determined experimentally using the following formula:

$$EC = \frac{Hv \times 1000}{v_1}$$

where EC is the exchange capacity\* of the cation exchanger, in g-equiv/cu.m;  $H$  is the hardness of water, in mg-equiv/litre;  $v$  is the quantity of water passed through the filter till the moment when first calcium ions appear in the filtrate (to 0.05 mg-equiv/litre), in litres;  $v_1$  is the volume of the cation-exchange resin, ml; 1000 is the conversion factor (for conversion of milligrams into grams, and from millilitres to cubic metres, or else from mg-equiv/ml to g-equiv/cubic metre).

It should be noted that the rate of the cation-exchange process depends on many factors, for example, on the valency of the ions, their charge, the degree of hydration, and the effective ion radius. With all other conditions being equal, polyvalent ions better exchange with sulphonated cation-exchanger than monovalent ions. The ions can be arranged by their decreasing capacity of entering the cation-exchanger as follows:  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ . This regularity can be changed by increasing the ion concentration and the phenomenon is used in the recovery of cation-exchangers by treating them with concentrated sodium chloride solutions.

Table 9.2 gives some characteristics of ion-exchangers.

A cation-exchange filter is a steel cylinder, from 1 to 3 m in diameter, in which a bed of cation-exchange resin is supported on a screen. The depth of a filter bed is 2-4 metres. The rate of liquid passage is from 4 to 25 metres per hour. The filters can work under a pressure up to 6 kg/sq.cm.

The work of a cation-exchange filter consists of the following stages:

- (1) filtration until the exchange capacity of the filter is exhausted;
- (2) loosening of the cation-exchange resin with an upstream current of liquid;
- (3) recovery of the filter with NaCl solution (for Na-cation exchange processes);
- (4) washing the charge from excess quantities of the recovering material.

The regeneration of the charge (items 2, 3, and 4) continues for 90-120 minutes.

The salt content of the water treated on a Na-cation exchanger is 0.05 mg-equiv/litre. A two-step Na-cation exchange process is normally used to purify water. Water undergoes coarse softening

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\* The exchange capacity is expressed in gram-equivalents of the ions retained by one cubic metre of the swollen ion-exchange resin.

Table 9.2

## Specifications of Some Ion-Exchange Materials

Ion exchanger	Functional group	Bulk weight* g/ml	Swelling coefficient	Granule, size, mm	Exchange capacity
<i>Cation exchangers</i>					
Glauconite		1.40	1.00	0.2-0.7	143
Sulphonated coal	— SO <sub>3</sub> H	0.60	1.30	0.3-2.0	400
KY-1**	— SO <sub>3</sub> H	0.70	1.80	0.3-2.0	1000
KY-2***	— SO <sub>3</sub> H	0.70	1.80	0.3-2.0	1500
<i>Anion-exchangers</i>					
Espatite TM		0.70	1.20	0.3-2.0	1000
Espatite ЭДЭ-10П	= NH; ≡ N; = N—C <sub>6</sub> H <sub>5</sub>	0.70	2.0	0.3-2.0	1500
AB-16	= NH; ≡ N; = N—C <sub>6</sub> H <sub>5</sub>	0.60		0.3-2.0	1000

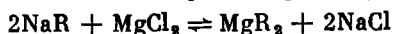
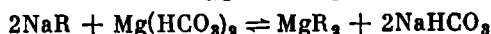
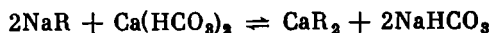
\* The bulk weight of ion-exchange resin is the weight of a unit volume of the resin comprising its pores and voids between separate granules.

\*\* KY-1 is the synthetic cation-exchange resin of high chemical strength. It is stable in an acid medium and stands the temperature to 90-95°C.

\*\*\* KY-2 is sulphonated coal. This cation exchanger is also stable in acid and alkaline medium at temperatures to 100°C.

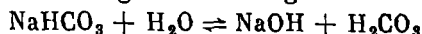
at the first stage when about 75 per cent of the initial hardness is removed. The residual hardness is removed by treatment on the second-stage filters. Since the main bulk of the calcium and magnesium ions is retained on the first-step filters, the load on the second-step filters with respect to hardness is not great and their working cycle can continue for 150-200 hours. The residual hardness of water after a two-step cation-exchange treatment is 0.01-0.02 mg-equiv/litre. This method saves salt for the regeneration of the first-step filters. Washing waters of the second-step filters are used for the purpose. Furthermore, the two-step Na-cation exchange process simplifies the operation of the plant to prolong the working terms of the filters without additional control of the filtrate.

The following processes occur during the cation-exchange process:



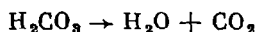
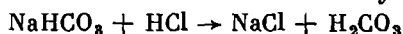
During filtration of waters with noncarbonate hardness, salts of strong acids and strong bases are obtained. These salts are not hydrolyzed even at high temperatures. But when carbonate hardness is removed, sodium hydrocarbonate is formed which is hydrolyzed

at high temperatures to give a strong alkali:



The alkalinity of water in boilers therefore strongly increases. Experiments show that the alkalinity of water in a boiler after eight hours of continuous work increases from 30 to 400 mg-equiv/litre. Water foams, begins splashing from the boiler, and can cause caustic embrittlement of the metal.

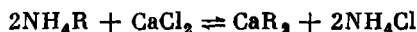
In order to decrease alkalinity of water, it is passed through Na- and then H-cation-exchange filters, or the current is divided into two streams, one of which passes through a Na-cation exchanger, and the other through the H-cation-exchanger after which the filtrates are mixed. A strong acid which is formed during H-cation-exchange treatment neutralizes the alkalinity of water:



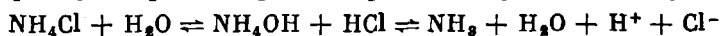
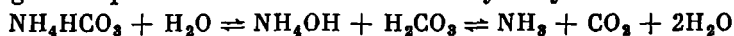
Carbon dioxide is then removed from the water. Sometimes, water is passed through a mixed filter consisting of Na- and H-cation-exchange materials.

Parallel filtration through ammonium-cation and Na-cation exchanger is commonly used.

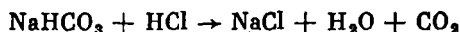
The ammonium-cationite treatment of water consists in its softening by filtering through a bed of a cation exchanger impregnated in exchange cations of ammonia  $\text{NH}_4^+$ . During this process, the scaling ions are exchanged for the ammonium ion:



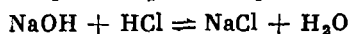
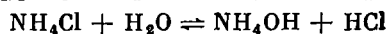
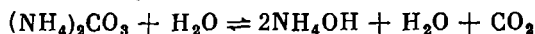
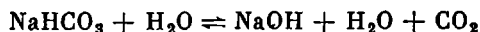
The salts  $\text{NH}_4\text{HCO}_3$ ,  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$  are formed in the filtrate. At high temperatures these salts are hydrolyzed:



Hence, the filtrate, after the ammonium-cationite treatment, reacts acid, while the filtrate after the treatment on a Na-cation exchanger reacts alkaline. When the two filtrates are mixed, they neutralize each other:



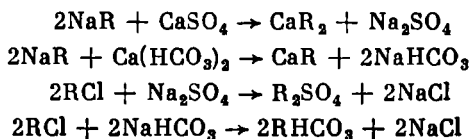
The combined treatment on Na- and  $\text{NH}_4$ -cation exchangers is practically used. Sometimes both cation-exchangers are loaded in one filter and later regenerated simultaneously as well. Thus obtained filtrate is neutralized in the boiler:



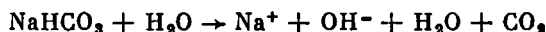
This method ensures any required alkalinity of water.

**Softening Water by Treatment on Na<sup>+</sup>- and Cl<sup>-</sup>-Ion Exchangers.** Water can be softened with simultaneous reduction of alkalinity by filtering through a bed of a mixture consisting of cation- and anion-exchange materials, or by successive passage of water through the filters. Sulphonated coal, strongly acid KY-1 or KY-2 are used as cation-exchangers and weakly basic AH-2Φ, or strongly basic AH-17 as anion-exchangers.

The following reactions occur when water passes the mixed ion-exchanger:



This method removes the HCO<sub>3</sub><sup>-</sup> ion responsible for high alkalinity of water in boilers because, at high temperatures, NaHCO<sub>3</sub> is hydrolyzed to give a strong alkali:

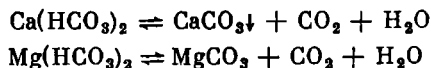


This method is only used to treat water for low-pressure boilers, evaporators, etc. It has some advantages over treatment of water on Na<sup>+</sup>- and H<sup>+</sup>-cation exchangers because it does not require additional reagents or protection of equipment from corrosion; the filtering material is regenerated by one reagent, sodium chloride, the equipment is easy to control and maintain. The disadvantage of the method is an increased content of the chloride ion in the treated water.

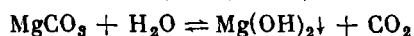
If water characterized by high hardness and turbidity should be thoroughly softened, use should be made of a combined method in which water is treated with reagents and on cation-exchangers. This method can remove salts from water practically to zero hardness.

Coarse disperse systems interfere with cation-exchange treatment of water. Suspended particles clog the pores in the cation exchanger to decrease its exchange capacity. The water becomes more aggressive after the treatment on the cation exchanger because the replacement of calcium hydrocarbonate by sodium hydrocarbonate frees equilibrium carbon dioxide.

**Thermal Softening of Water.** When water is heated to boiling, calcium hydrocarbonate and magnesium hydrocarbonate are converted into carbonates as follows:



These reversible processes can be completely shifted to the right by boiling water since the solubility of carbon dioxide decreases at high temperatures. But it is impossible to completely remove the carbonates because calcium carbonate is slightly soluble in water (about 9.95 mg/litre at 15°C). The solubility of  $\text{MgCO}_3$  is sufficiently high (110 mg/litre) and after a prolonged treatment it is hydrolyzed to form a sparingly soluble (8 mg/litre) magnesium hydroxide:



Sulphates are usually removed by boiling since the solubility of calcium sulphate falls with increasing temperature. This method can be used to soften water containing mainly carbonates and intended for low- and medium-pressure boilers.

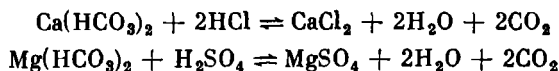
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## 9.10. Acidifying

Carbonates contained in hard water can be converted into noncarbonates by mineral acids.

Many industries require that the water for technical purposes should not contain carbonates, while the presence of noncarbonate salts is admissible. For example, hard water used for cooling can precipitate calcium carbonate onto the apparatus walls if the temperature drop is high. Since water will not evaporate in these conditions, salts other than carbonates will not be precipitated either.

Water is treated by hydrochloric or sulphuric acid which is added in quantities equivalent to the hardness caused by the presence of carbonates. The following reactions occur



Water treatment by acidification is convenient because no special reagents are required, the chemical reaction is very fast, and no substances precipitate. The disadvantage of the method is its high cost and the necessity of a thorough control of quantities of the added acid. The process can however be controlled automatically by measuring the electrical conductivity of the water (the increased conductivity indicates the presence of free acid).

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## 9.11. Desalting Water

The process by which salts are removed from water is called *desalting*. Depending on a particular technique used for the purpose, almost all salts can be removed from water or their residual content can be 1000 mg/litre. This may be done by (1) distillation or freezing

out, (2) electrochemically, or (3) by the ion-exchange method.

**Distillation and Freezing Out.** To *distil water* it is heated to boiling and the steam is passed to a condenser, from which the distillate is collected in a receptacle. The method is suitable to remove non-volatile substances.

If the salts are separated from water by *freezing out*, a concentrated solution is frozen and the first portions of ice are pure solvent containing only negligible amounts of the dissolved salts, which however melt first when the temperature is raised.

Electrochemical desalting water is based on the *electrodialysis* and *electroosmosis* phenomena\*.

The mechanism of electrochemical desalting of water consists in the electrolysis of salts present in the water by passing electric current through it. The anions are oxidized at the anode and the cations are reduced at the cathode in this process. The cathode and the anode spaces are isolated from the main current by diaphragms (Fig. 9.13). The anode diaphragm is ceramic or micro-porous rubber, while the cathode diaphragm is asbestos cloth. A magnetite electrode ( $\text{Fe}_3\text{O}_4$ ) is placed in the anode chamber and an iron, zinc, or steel electrode is placed in the cathode chamber.

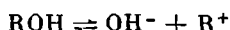
Water is fed into the central chamber and when electric current is passed, the ions penetrate the diaphragms to get into the anode or the cathode chambers. Their back diffusion is prevented by the diaphragms. A common apparatus for desalting water consists of a battery of ten cells connected in series. Water passes the cells one after another and becomes more and more desalted. The potential between the electrodes in the first cell is low, but it gradually increases in subsequent cells to attain the mains voltage (110-120 V, d.c.). The energy consumption depends on the mineralization degree of water and varies from 1.5 to 4.5 kW·hr per 100 litres of purified water.

A three-compartment dialysis cell cannot be used to treat waters because the diaphragms become clogged with calcium carbonate and the unit should be recovered by acid treatment. The diaphragms in the first cell become clogged especially hard. To remove this difficulty, divalent and monovalent ions can be removed separately. Only anions are removed in the first cells, while divalent cations precipitate as hardly soluble salts due to the lowered concentration of the hydrogen ion. Two-compartment cells with only one diaphragm are used for the purpose. Salt water is fed into the cathode compartment where polyvalent cations precipitate. Next alkaline metals are removed in three-compartment cells. Their diaphragms are now soiled to a lesser extent.

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\* Electrodialysis is diffusion of electrolytes through a porous partition under the action of electric current. Electroosmosis is the movement of liquid in pores of the diaphragm under the action of electric current.

Porous ion-exchange diaphragms are used for practical water treatment. These are thin flexible plates manufactured from an inert carrier which support cation-exchanger (cation-exchange diaphragm), or anion-exchanger grains (anion-exchange diaphragm). When the diaphragms are immersed in water, the ion-exchangers dissociate and the exchanged ions pass in solution



The anion-exchange diaphragm is charged positively and the cation-exchange diaphragm, negatively.

The unit for water desalting by this method is a battery of cation- and anion-exchange diaphragms arranged as shown in Fig. 9.14. A potential difference is applied across the end plates *c* and *d*, and the cations move toward the cathode and the anions toward the anode.

The cations will leave all even-numbered cells to enter (through the negatively charged cation-exchange diaphragm, *a*) the cell neighbouring on the left, while the anions (through the positively charged anion-exchange diaphragm *b*) will pass into the cell neighbouring on the right. The ions are held back from the return to the even-numbered cells by the anion-exchange diaphragms. The even-numbered cells are connected by a pipe-line *III* through which deionized water is discharged from the unit, while all odd-numbered cells are connected by the pipe-line *II* through which mineralized water is withdrawn.

Ion-exchange diaphragms preclude the diffusion processes and increase the yield of deionized water. The electrochemical units can be used to treat highly mineralized waters (even sea water containing to 30 g/litre of salts).

**Ion-Exchange Method.** The method consists in passing water through H- or OH-form ion-exchange filters. The following processes

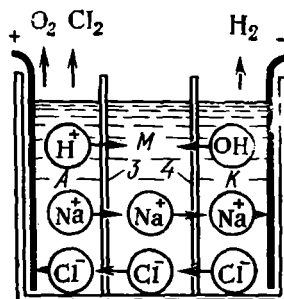


Fig. 9.13. Desalting water in a three-chamber electrolyser

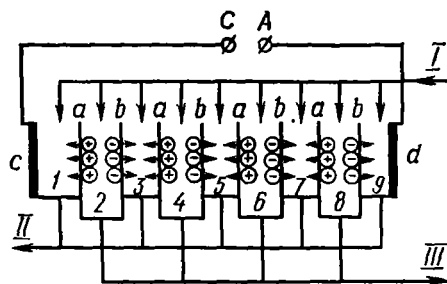
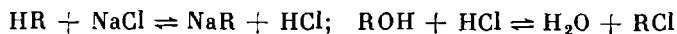


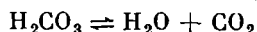
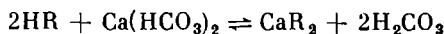
Fig. 9.14. Desalting water in a diaphragm-type unit:

*a*—cation-exchange diaphragms; *b*—anion-exchange diaphragms; *c* and *d*—metal plates to which a potential difference is applied

are involved:



or



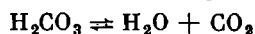
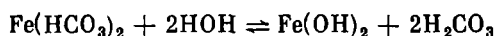
Carbon dioxide is removed by degasification, either by bubbling air through the water, or by spraying water in towers.

The H-cation charge is regenerated with a 1-1.5 per cent solution of sulphuric acid or a 3-7 per cent hydrochloric acid. The anion-exchange filters are regenerated by 4-5 per cent solution of NaOH or  $\text{NaHCO}_3$ . This method ensures the purification of water to 10-15 mg./litre of residual salts.

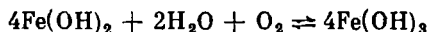
## 9.12. Removal of Iron, Manganese, Silica and Fluorine From Water

**Removal of Iron and Manganese.** The method of removal of iron from water consists in oxidation of divalent iron to trivalent metal and its precipitation as ferric hydroxide.

If iron is contained in water as hydrocarbonate, it can be removed by aeration. This salt, formed by a weak acid and a weak base, is hydrolyzed as follows:

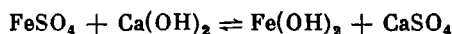


Carbon dioxide is removed from water by aeration, and the hydrolysis can therefore be completed to the end. Ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ , is oxidized by atmospheric oxygen into  $\text{Fe}(\text{OH})_3$  by the following reaction:

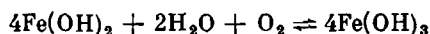


The method can be used to reduce the iron content up to 0.1-0.3 mg./litre. Humins interfere with precipitation of iron, since they are protective colloids with respect to ferrous hydroxide. Chlorine is used in such cases to treat water. Chlorine oxidizes ferrous iron to ferric iron and destroys the humins.

Ferrous sulphate is removed from water by treating it with lime:



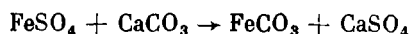
and further



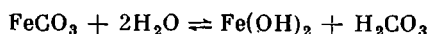
L. A. Kulsky recommends to remove iron, manganese and silica by a mixed coagulant consisting of sodium aluminate and ferric

chloride (the optimum molar ratio of  $\text{NaAlO}_2$  to  $\text{FeCl}_3$  is 1 : 1). The concentration of residual iron does not exceed 0.3 mg/litre. Iron contained in organic and inorganic compounds can be removed by this method.

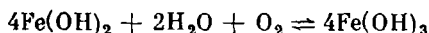
Another method to remove iron is to pass water through a bed of highly dispersed suspension of chalk and aluminium hydroxide. The iron salts are converted by chalk into ferrous carbonate:



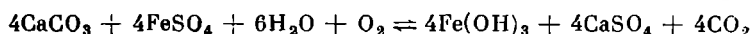
which is hydrolyzed into ferrous hydroxide:



and the divalent iron is then oxidized to trivalent metal:

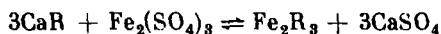


The reactions can be expressed by the following overall equation:



Ferric hydroxide is retained in the suspended filter which contains 16 parts by weight of  $\text{Al(OH)}_3$  per 100 parts of  $\text{CaCO}_3$ . The velocity of the upstream current through the suspended filter is from 0.15 to 0.48 mm/sec. About 95 per cent of iron contained in water can be removed by this method.

Ferric ion can be removed from water by the cation-exchange method. For example, when water passes through a calcium form of the cation-exchanger, the following occurs:



The iron content can be decreased by this method up to 0.05 mg/litre and lower.

The investigations carried out in the USSR have shown that ferrous iron is converted into ferric iron when water passes through a granular filter (without preliminary oxidation of iron). The process is accompanied by formation of a ferric oxide film on the grains of the filter, which acts like a catalyst. Hence, the purification of water from iron by filtration is an autocatalytic process.

There is no universal method to remove iron from subsoil water, and the selection of a particular method depends on the analysis of water taken from the source.

The removal of iron from subsoil sources by filtration is combined with one of the methods for preliminary purification of water: simplified aeration, aeration, adding oxidants with or without aeration.

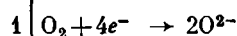
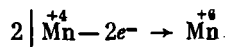
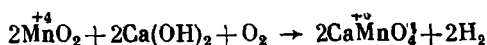
The simplified aeration consists in that water falls on the filter from a height of 0.5-0.6 m. The method is convenient for waters containing to 10 mg/litre of total iron, of which the ferrous iron content should be not less than 70 per cent since no film is formed on the grains in its absence. This method is inapplicable to waters containing hydrogen sulphide and carbon dioxide, large amounts

of oxygen demanding wastes and if the pH is low. The oxygen content should be optimum (0.6 mg/litre for some waters) because its excess or deficit deteriorates the process of iron removal. If free carbon dioxide content of water is above 50 mg/litre no ferrous film is formed on the grains since all ferrous iron is in the form of a soluble salt  $\text{Fe}(\text{HCO}_3)_2$ . The presence of  $\text{H}_2\text{S}$  in water binds dissolved oxygen. This also interferes with normal formation of the film. At low pH, ferrous iron is quickly oxidized to ferric iron.

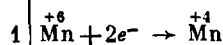
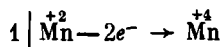
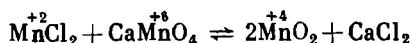
The investigations have shown that only the presence of ferrous iron in water delivered on the filter provides the conditions under which the film is formed to ensure the high iron-removal effect. For example, if water contains only ferrous iron, the film is formed in 5.5 days, while if its content is only 64 per cent of the total iron in water, the film is formed in 12 days. The film will not be formed altogether if the water does not contain ferrous iron.

At the present time, the investigators have developed a method of iron removal from subsoil waters. They studied the conditions for simplified aeration, and established the necessity of charging the filter bed, and determined the wide range of application of this method to treatment of such waters.

Manganese is removed from water by oxidation of the divalent ion into tetravalent. This cannot be done by atmospheric oxygen and a more energetic oxidizer is required. Water is treated with lime in the presence of pyrolusite or quartz sand with  $\text{MnO}_2$  film applied onto its grains. Atmospheric oxygen oxidizes manganese in an alkaline medium from its tetravalent state to hexavalent manganese since the oxidation potential of conversion of  $\text{MnO}_2$  to  $\text{MnO}_4^{2-}$  is 0.60 V, while that of dissolved oxygen is 0.83 V. The process can be described by the following equations:



Hexavalent manganese oxidizes divalent manganese to its tetravalent state as follows

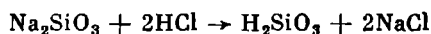


The oxidation potential of the conversion of  $\text{Mn}(\text{OH})_2$  into  $\text{MnO}_2$  in an alkaline medium is 0.05 V.

Manganese can be removed from water by oxidation on filters with  $\text{MnO}_2$  films obtained by treating sulphonated coal with 1.2-3

per cent solution of  $\text{KMnO}_4$ . The charge is regenerated with a 0.25 per cent solution of  $\text{KMnO}_4$ .

**Removal of Silicic Acid.** Silicic acid can be removed from water by *acidifying* with hydrochloric or sulphuric acid:



The colloidal solution of silicic acid is then coagulated with sodium aluminate  $\text{NaAlO}_2$ . The method requires accurate dosage of mineral acid since even slight overdosage can cause corrosion of the apparatus.

Part of silicic acid is removed as sparingly soluble salts  $\text{CaSiO}_3$  and  $\text{MgSiO}_3$  when water is softened by the *soda-lime* method.

$\text{H}_2\text{SiO}_3$  is removed by the mixed coagulant as well.

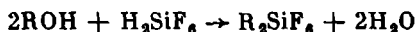
There exists another method to remove silicic acid. It is based on the ability of calcined magnesia, dolomite, and magnesite to sorb silicic acid from water. The method is very effective and the consumption of the reagents is low if the process is carried out with heating.

Silicon can be completely removed from water if it is passed through strongly basic anion-exchange filters.

Silicic acid can be removed by hydrofluoric acid with subsequent filtration through weakly basic ion-exchangers:



$\text{H}_2\text{SiF}_6$  is a strong acid which can easily be trapped by weakly basic ion-exchange filters:



The ion of metasilicic acid is removed also by deionizing water with  $\text{ЭДЭ-10П}$  and  $\text{AB-17}$  anion-exchange resins.

**Fluorination and Defluorination of Water.** When in small quantities, fluorides are a vital necessity for man and animals. Fluorine is a component part of bones and teeth. Tooth tissues contain about 0.02 per cent of fluorine, its major part being in tooth enamel whose composition is close to the formula  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ . But excess fluorine in water or air (as dust) is poisonous since all fluorine compounds are poisons. Fluorine poisoning destroys enamel of the teeth, and makes the bones brittle. Fluorine is accumulated in the body even if it is introduced in small doses. Chronic poisoning with fluorine manifests in the loss of appetite, cachexia, structural changes in the bone tissues and teeth. It affects the joints, kidneys, liver, heart, adrenal glands, testes, and thyroid gland.

It is supposed that fluorine destroys the enzymes involved in the metabolism (possibly due to combining with metals such as Cu, Fe, Mn, Zn and others which are part of the enzymes).

Surface waters contain insignificant quantities of fluorine measured by tenth fractions of a milligram per litre. But subsoil waters,

from artesian and other wells, and also from springs, which are used for local water supply, contain increased doses of fluorine, its concentration rising as high as to 6-10 mg/litre. Fluorides enter the human and animal body mainly with water.

The vast investigations in the USSR and abroad have brought the specialists to a conclusion that the absence of fluorine in water causes the caries of the teeth.

Waters containing increased doses of fluorine should be defluorinated and, on the contrary, fluorine-poor waters should be fluorinated.

*Defluorination of Water.* Water is defluorinated by binding fluoride ion with chemical reagents, or by its sorption on various materials. Methods of binding the fluoride ion with salts of aluminium, magnesium, and phosphoric acid have been studied as well.

When water is treated with *aluminium sulphate*,  $\text{Al}_2(\text{SO}_4)_3$ , fluorine forms a sparingly soluble  $\text{AlF}_3$ , which is precipitated together with aluminium hydroxide. The dose of aluminium sulphate required to defluorinate water depends on the pH of the medium. If the solution reacts neutral, the consumption of  $\text{Al}_2(\text{SO}_4)_3$  is 30-40 times higher than with an acid medium (pH from 4.3 to 4.8).

The process therefore requires preliminary acidification of water with subsequent alkalyzing after defluorination, which makes the process complicate and expensive. R. D. Gabovich has calculated the doses of the reagents required to defluorinate waters with various initial fluorine concentrations (Table 9.3). Defluorination with aluminium sulphate in an alkaline medium does not require subsequent alkalyzing.

Table 9.3

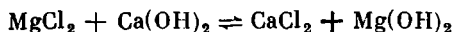
Defluorination of Water by Treatment with  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Na}_2\text{CO}_3$  (total hardness, 1.78 mg-equiv/litre, carbonate, 1.24 mg-equiv/litre)

Fluorine concentration in water before treatment, mg/litre	Reagent dose, mg/litre		Fluorine concentration in treated water, mg/litre
	$\text{Al}_2(\text{SO}_4)_3$	$\text{Na}_2\text{CO}_3$	
2	300	150	0.72
2	500	250	0.40
4	500	250	1.22
6	500	250	1.50
6	1000	500	0.77

The tabulated data were obtained for the time of contact of water with the reagents of 4-6 hours. During this time all suspended matter precipitates and the clarified water contains residual fluorine in concentrations specified in Table 9.3.

The dose of sodium carbonate depends on the presence in water of carbonate hardness: the higher the hardness, the smaller amounts of soda are required. For example, if the dose of aluminium sulphate is 800 mg/litre and the hardness is 5 mg-equiv/litre, the required dose of soda is 300 mg/litre; if the hardness is 7 mg-equiv/litre, the required dose of soda is 100 mg/litre, and if 9 mg-equiv/litre sodium carbonate is not required at all.

Defluorination of water with *magnesium salts* is carried out with adding lime which increases the pH of the water to 10.2-10.3. Magnesium hydroxide is formed in these conditions:



It is supposed that magnesium hydroxide reacts with the fluoride ion to form an insoluble basic fluoride (oxyfluoride) of magnesium which precipitates:



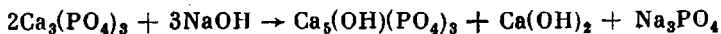
According to the data provided by Vodgeo\*, the fluorine concentration can be decreased by this method from 5 to 1 mg/litre.

The consumption of magnesium salts ( $G_{\text{Mg}}$ ) can be determined by the formula

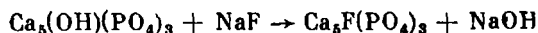
$$G_{\text{Mg}} = [2(c_F - 1) - H_{\text{Mg}}] E \text{ mg/litre}$$

where  $c_F$  is the initial fluorine concentration in water, in mg/litre; 1 is the concentration of the residual fluorine, mg/litre;  $H_{\text{Mg}}$  is the hardness of the water due to magnesium, mg-equiv/litre; and  $E$  is the equivalent mass of the magnesium salt.

Water can be defluorinated by *calcium phosphate* which binds fluorine into a sparingly soluble compound. Calcium phosphate should preliminarily be treated with a 10 per cent solution of NaOH during which calcium oxyphosphate is formed:



This calcium salt binds the fluoride ion according to this equation:



The reaction proceeds better in a weakly alkaline medium and is recommended for fluorine concentrations not less than 10 mg/litre.

According to Vodgeo, the consumption of tribasic calcium phosphate is about 10 mg per one mg of removed fluorine.

**The Sorption Method.** Strongly basic anion-exchange resins, special activated coals, magnesia sorbents, and activated alumina can be used to extract fluorine from water.

The best material is activated alumina. It is obtained from commercial alumina by two-fold calcining at 800°C, with intermediate cooling and wetting with a 15 per cent soda solution. The depth of

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\* National Research Institute for Water Supply and Sewage.

the sorbent bed in the filter should be about 2 metres. The working exchange capacity (according to Vodgeo) is 1.25 kg of fluorine per cubic metre of the sorbent.

The alumina is regenerated with a 2 per cent solution of sodium hydroxide with subsequent neutralization of excess alkali with a 0.5 per cent solution of hydrochloric acid. The investigations show that activated alumina reacts with fluoride ion to retain it on its surfaces.

*Fluorination of Water.* To fluorinate water, salts containing the fluoride ion are added to it. Sodium fluoride,  $\text{NaF}$ , is added as a 2-3 per cent solution or as a dry substance; sodium fluosilicate,  $\text{Na}_2\text{SiF}_6$ , is added in the dry form because of its poor solubility. Fluosilicic acid,  $\text{H}_2\text{SiF}_6$  and hydrofluoric acid,  $\text{HF}$ , are added in solution form. Flural,  $\text{AlF}_3 \cdot \text{H}_2\text{O}$ , ammonium fluosilicate,  $(\text{NH}_4)_2\text{SiF}_6$ , and other reagents are also used for fluorination of water.

In order to avoid overdosage of fluorine, the reagents added to water should be accurately measured. According to the sanitary requirements, the fluorine content of water should not exceed 1.5 mg/litre and be less than 0.7 mg/litre. The required fluorine doses are determined experimentally for each particular water, i.e. by test fluorination. Waters which do not contain fluoride ion, are fluorinated with a dose of about 1 mg/litre in winter and of about 0.7 mg/litre in summer. The decreased concentration of the fluoride ion in summer is explained by that greater amounts of water are passed through the human body in the hot season.

Water is fluorinated now in most countries of the world. In the USSR it is fluorinated whenever the need arises.

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### 9.13. Purification of Water From Radioactive Substances

Natural waters can contain radioactive substances of natural and artificial origin. Natural radioactivity is given to water when it passes rocks rich in radioactive elements (the isotopes of uranium, radium, thorium, potassium, and others). Artificial radioactivity of water is due to its contamination with industrial radioactive wastes, and wastes from medical and other institutions engaged in radioactive research. Natural water can also be contaminated with radioactive elements by experimental underground nuclear explosions.

Sewage of increased radioactivity, 100 Cu and over, is buried in special containers or pumped into underground cavities which are not communicated with water bodies.

Radioactive substances are accumulated in the plant and animal tissues and can be transmitted to man by the trophic chain (e.g. through taking fish as food). Radioactive substances can be concentrated in small organisms which are used as food by larger animals, beasts of prey, etc., in whom they are accumulated in dangerous concentrations. Radioactivity of some plankton organisms 1000 times increases the radioactivity of the water. Some fresh-water fishes which are one of the most important links in the trophic chain, are 20-30 thousand times more radioactive than the water where they live. When the organisms die, they become the source of the secondary radioactive contamination of water.

In the USSR, all possible measures are taken to protect the sources of water supply from radioactive contamination. If however any radioactive waste gets into water by accident, the use of water from this source is temporarily suspended.

Water can be decontaminated by two methods:

- (1) water can be kept for a time required for the short-lived isotopes to decay, and only then delivered to the consumer;
- (2) all suspended or dissolved radioactive substances are removed from the water.

Radioactive substances can be removed from water by distillation, settling, filtration, coagulation, adsorption (on sand, clay, active carbon, metals, and other adsorbents), by ion-exchange processes, and also by various combinations of the mentioned methods.

If radioactive contaminants are suspended in water, they can be removed by settling. The time of settling of short-lived isotopes is determined by the half-life period of a particular contaminant. Suspended radioactive particles are absorbed by microorganisms of the biological film on slow-filters. Common sand filters retain only part of radioactive contaminants since the adsorbing capacity of quartz sand is low. The percentage of radioactive substances that can be retained by various filtering materials is as follows: quartz sand, 72-89; activated alumina, 94; charcoal, 86; activated carbon, 92; and glauconite, 83.

Fine dispersions of radioactive substances are removed by coagulation. Coagulants and their doses are selected experimentally. As a rule, the dose of the coagulant is slightly higher than required theoretically. For a better coagulation, the water is alkalyzed, and the concentration of the element in question is increased by adding the corresponding nonradioactive isotope. This ensures the required inactivation of water. Aluminium sulphate, ferric sulphate, ferric chloride, phosphates ( $\text{Na}_3\text{PO}_4$  and  $\text{KH}_2\text{PO}_4$ ), lime with activated sodium silicate, polyelectrolytes and other substances can be used as coagulants.

The coagulation is more effective if water is turbid. To that end, from 1 to 4 g/litre of clay is added to contaminated water and it is

alkalized to pH 11. In 100 minutes of the contact, the radioactivity of water decreases 90 per cent.

Powdered iron taken in a dose of 1000 mg/litre is used for decontamination of water. The time of contact is 90 minutes.

The products of radioactive decay are adsorbed by aluminium, zinc and copper. In some countries water is therefore filtered through a bed of metal chips (0.5-0.8 m deep). This removes about 80-85 percent of radioactivity. The filter is regenerated by hydrochloric acid.

Some radioactive isotopes  $^{89}\text{Sr}$ ,  $^{140}\text{Ba}$ ,  $^{140}\text{La}$  and  $^{115}\text{Cd}$  can be removed by water softening with lime-soda but increased reagent doses are required.

The maximum allowed concentrations of radioactive substances in water of open bodies and sources of water supply can be found in the "Protection of Surface Waters from Contamination with Sewage" (issued by the Ministry of Land Reclamation and Water Management of the USSR, Moscow, 1974).

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## 9.14. Magnetic Treatment of Water

The magnetic treatment of water in this country is done in accordance with the investigations carried out at the Kharkov Engineering and Economics Institute, the Kazakh University, the Novoçerkassky Polytechnical Institute and many other institutes and plant laboratories.

The vast research shows that the most appreciable changes in the properties of magnetically treated water occur in the presence of impurities. The changes are especially marked at the interface between the solid and the liquid phases.

Magnetic treatment of water gives the following physico-chemical changes: (1) acceleration of the coagulation process; (2) changes in the process of salt crystallization (salts are not crystallized on the apparatus walls but in the bulk of the system); (3) changes in the wetting of solid surfaces; (4) acceleration and intensification of the adsorption processes; (5) acceleration of dissolution of inorganic salts; (6) changes in the concentrations of dissolved gases.

In all cases, in order to ensure the appreciable effect, it is necessary that a magnetic field of certain intensity should be applied, and the flow rates of water or suspensions should be strictly controlled. The effect of magnetic treatment is less marked if the process is effected in stationary conditions.

Dense precipitates, which are difficult to remove, are formed during coagulation. This can probably be explained by the changes occurring in the water and the suspension. Water molecules probably are not strongly connected with the suspension and the particles can thus move toward each other to a distance at which van der Waals'

forces become effective. These forces promote aggregation of the particles.

The formation of crystalline structures in the bulk of the system has been used in the invention of T. Vermayern, who treated water magnetically to decrease scale deposition on the walls of boilers. The conditions of magnetic treatment (field intensity and flow rate) should also be strictly controlled depending on the type and concentration of impurities in water. The literature contains indications that magnetic treatment changes the crystalline structure of a substance; for example, aragonite rather than calcite is precipitated from a magnetically treated water.

Magnetic treatment of water intensifies adsorption of surface active substances on both solid surfaces and at the interface between the liquid and the air. The rate of dissolution of inorganic salts increases dozens of times (120 times for  $\text{MgSO}_4$ ) if the direction of the magnetic field sharply changes.

The concentration of dissolved oxygen increases in magnetically treated water. It indicates to elasticity of the intermolecular bond in the structure of associations which are formed by the deformation of the hydrogen bond under the action of a magnetic field.

The investigators point out the great effect of impurities (in the form of nonelectrolytes and gases) on the structure of water. These substances are dissolved in two steps: cavities of the corresponding size are first created in water, and then the molecules of the solute are incorporated into them. Depending on the size, the solute molecules enter the cavities of the framework of liquid water associations to stabilize or destroy it.

The literature contains indications of bactericidal action of magnetic treatment. First positive results of using magnetically treated water for medical purposes have been reported.

Many hypotheses have been suggested to explain various factors induced in water by magnetic treatment. They can be classified as follows:

(1) 'colloidal' hypotheses based on the action of magnetic field on colloidal particles having high magnetic susceptibility (para- or ferromagnetic);

(2) 'ionic' hypotheses based on the action of magnetic fields on ions moving in water. Many researchers emphasize the effect that magnetic fields have on ion hydration. Magnetic treatment decreases the hydration of ions. This is confirmed by the sorption capacity of ion-exchange filters which increases 20-40 per cent compared with nonmagnetically treated water);

(3) 'aqueous' hypotheses explaining the action of magnetic fields on water proper. The angle between the lines connecting the hydrogen atoms with the atoms of oxygen (*ortho*- and *para*-positions of hydrogen) is changed in magnetic field.

Processes that occur in water during its magnetic treatment are quite varied and complicated, and this explains why the scientists are not yet unanimous in explaining the mechanisms of these phenomena.

## CHARACTERISTICS OF MUNICIPAL AND INDUSTRIAL SEWAGE

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### 10.1. Origin of Impurities

Effluent waters, which should be removed from settlements and industrial enterprises, are known as *sewage*. Used water which does not require considerable purification is regenerated and reused. This is the *return water*.

Effluents are classified by their origin as domestic or public sewage, industrial effluents, and atmospheric (rain) runoff. Depending on the degree of pollution and the sanitary requirements, all effluents can be either discharged straight into a stream or only after the appropriate treatment (mechanical, chemical, biological).

Public (municipal) sewage consists of waters containing food wastes, various washings and laundry wastes, waters from lavatories, baths, etc. These waste waters are unstable polydisperse systems. Their particles can be coarse and very fine (molecules and ions). A 5-day BOD of these waters varies from 100 to 400 mg/litre (data supplied by courtesy of Vasilevski Ostrov Water Pumping and Treating Plant in Leningrad).

The composition of public sewage is relatively constant. The origin of the pollutants is clearly connected with the human metabolism and vital activities. All the pollutants are mostly organic, of vegetable and animal origin. Inorganic impurities are sand, clay, particles of ore, slag, chalk, mineral salts, mineral oils, and many other substances which are used by man for various purposes.

Public sewage contains various microorganisms; bacteria, yeast and other moulds, algae, eggs of helminths, viruses, etc. These effluents are dangerous with respect to epidemic diseases of man and animals since in addition to saprophytic they contain all pathogenic organisms infesting man.

S. N. Stroganov treated statistically the data concerning Moscow sewage in 1903-1922 and derived an empirical formula to determine the concentration of pollutants in municipal sewage ( $c$ , in mg/litre):

$$c = \frac{a 1000}{g}$$

where  $a$  is the amount of pollutants of a given type per capita a day;  $g$  is the standard daily requirement of man for water; 1000 is the conversion factor from grams to milligrams.

The composition of daily sewage for one man are as follows:

Pollutant	g/g
Suspended matter	65
Ammoniacal nitrogen (N)	8
Chlorides	9
Phosphates	1.7
total BOD of settled sample	40

Using the above formula one can determine the amount of sewage  $g$  and the amount of a given pollutant  $a$  per capita a day.

**Example.** Determine the total BOD of sewage if the daily sewage per capita is 300 litres and the total BOD is 40 g per capita a day.

*Solution.*

$$c = \frac{40 \times 1000}{300} = 133 \text{ mg/litre}$$

**Runoffs** are due to atmospheric precipitation, i.e. due to rains, thawed snow, street washing, and other drain waters. Atmospheric precipitation is polluted with organic and mineral substances contained in the air, on the surfaces of various ground objects, and the soil, with which it comes in contact.

**Industrial sewage** is formed at industrial enterprises where water is used for various processes, and also for washing and rinsing of various apparatus, equipment, rooms, utensils, etc.

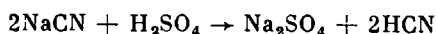
The composition of industrial sewage is quite varied, and special methods of its treatment are required for each particular case. For the sake of clarity, below follows a short description of two types of industrial sewage, viz., metal-plating and leather tanning plant sewage.

**Metal-Plating Sewage.** It contains poisons (cyanides, copper, chromium, etc.), whose concentration is seldom below 10 mg/litre. Sometimes, if the electrolyte is not allowed to drip off the article before its washing, the concentration of poisons can rise up to as high as 1000 mg/litre. Cyanides of alkaline metals are especially poisonous. Their 1 mg per kg body weight is a lethal dose.

The composition of the sewage at a metal-plating shop varies depending on the particular process. Three types of sewage are distinguished: (1) sewage containing simple and complex cyanides; (2) sewage containing metals in acid solutions; (3) sewage containing chromic acid.

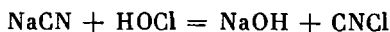
It has been established that sewage of all types should preferably be drained and treated separately from one another. Therefore enterprises engaged in chrome-plating and dealing with cyanides and acid electrolytes should discharge their wastes through three separate drains. The violation of this requirement interferes with normal work of sewage treatment plants and endangers the personnel. It is especially dangerous to mix together the cyanide and acid

sewage because an exchange reaction occurs with the liberation of hydrocyanic acid:



Hydrocyanic acid boils at 26°C and its vapour poisons the air.

Sewage containing cyan is treated with chlorine in an alkaline medium:

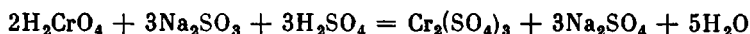


Cyanogen chloride is hydrolyzed in an alkaline medium:

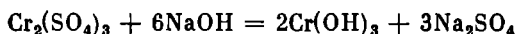


At pH 10 and in the presence of excess chlorine, cyanic acid is decomposed to give carbon dioxide and nitrogen ( $2\text{HCNO} + 3\text{Cl}_2 + 2\text{H}_2\text{O} = 2\text{CO}_2 + \text{N}_2 + 6\text{HCl}$ ) in a few minutes (the amount of chlorine consumed should exceed the cyan content more than three times). Complex compounds of zinc, cadmium and copper are decomposed in a similar way.

Sewage containing chromic acid is treated with sulphurous acid or sulphites. The reaction is as follows:



The sewage is then alkalyzed with NaOH with the liberation of chromium hydroxide:



Chromium hydroxide is amphoteric and precipitates only at pH from 7.5 to 9.5.

Acid sewage is neutralized with milk of lime or sodium hydroxide taken in quantities sufficient to adjust the pH to 7.5-9.5.

*Tannery Sewage.* These waste waters are dangerous because they can contain the causative agent of anthrax. The sewage is dangerous to the personnel of the plant and if discharged to open water bodies it can present danger to cattle as well.

The causative agent of anthrax is characterized by a very high adaptability and resistance to various chemical and physical actions. They can stand the temperature of 100°C for a considerable period of time. Common disinfectants, such as chlorine and its derivatives, formaldehyde, acids, corrosive sublimate, etc., can destroy these harmful microorganisms only on prolonged contact and only with high concentrations of the disinfectant (for example, the required dose of chloride of lime, according to the literature, is 16 kg per cubic metre of sewage). The problem of decontamination of tannery sewage has not therefore been fully solved. It is supposed that chloramine,  $\text{NH}_2\text{Cl}$ , destroys the causative agent of anthrax. Its concentration should be 20 mg/litre and the time of exposure not less than 60 minutes.

Anthrax spores preserve their harmful action even after a prolonged residence in soil or sludge and can cause the disease. The

sewage of leather tanning plants should therefore be regarded as infected and given the appropriate treatment with the disinfectants.

The chemical composition of leather tanning sewage is varied. Alkali prevails in the sewage of the chrome leather manufacture. Some shops discharge acid sewage.

A 5-day biochemical oxygen demand of spent tanning solution is 4340-5730 mg/litre.

The sewage of ash shops contains much free lime and sodium sulphite. Moreover, it contains wool and soluble organic substances.

According to H. Wagner (1950), the sewage of a tannery discharged after treatment of one ton of hide is equivalent to public sewage of a little town inhabited by 5000 people.

The effect that leather tanning industry has on the open water bodies is very great and often quite detrimental. The presence of sodium sulphite, chromium, and some tanning agents remove oxygen from water, give it an unpleasant odour, and practically completely stop the self-purification process in water bodies and kill the biota.

Leather tanning sewage is treated on the plant site. The sewage is first passed through eliminators, coarse screens to separate large objects. Wool is removed from the sewage in special wool traps. The suspended matter which passes the coarse screens is separated in horizontal settling tanks, where about 60 per cent of the suspended matter can be separated. The sediments are dehydrated on sludge sites or by centrifuging.

Raw skins are disinfected by a solution containing 2 per cent of hydrochloric acid and 15 per cent of common salt, in which they are kept at a temperature of 30°C for 40 hours (pickling). The floor and the walls of the main leather tanning shop are washed with water, and the waters, as well as the floor and the walls are treated with chloride of lime to kill the spores of the anthrax causative agent. The time of contact is 12 hours. The sewage from showers and sinks is boiled for at least one hour, the liquid is then cooled and disposed of into the sewer.

After preliminary treatment, the sewage of leather tanning shops is discharged into the municipal sewer and treated together with the main bulk of the sewage.

Ceramic tubes are recommended to drain the sewage of leather tanning industry.

The varied composition and quantities of sewage involves the necessity to apply different methods of treating it and the measures to prevent pollution of water bodies.

Improper treatment of sewage interferes with self-cleaning of water bodies by biological, chemical, and physico-chemical processes.

Industrial sewage containing fats or oils can form films on the surface of an open water body to insulate the water from its contact

with the air to change the oxygen conditions in the water body. Mineral oils are especially dangerous in this respect since they are difficult to decompose while vegetable oils and fats undergo biochemical decomposition much easier.

The harmful effect of sewage can be due to the presence of wastes of chemical industry, dyes, tanning agents, and also resins, the wastes of thermic processing of fuels. These substances also consume oxygen and give unpleasant organoleptic properties to water.

Dissolved inorganic substances contained in industrial sewage (mineral acids, hydrogen sulphide, alkalies, sulphides, sulphites, thiosulphates, salts of heavy metals) undergo chemical changes in open water bodies and this often involves partial or complete disappearance of oxygen in water and kills fish.

The degree of water pollution is assessed by sanitary and chemical analysis.

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## 10.2. Sanitary-Chemical Analysis of Sewage

Analysis of sewage differs from analysis of natural waters.

A sample of sewage should be analyzed on the day when it is taken. The following parameters are determined: (1) temperature; (2) colour; (3) odour; (4) clarity by reading characters; (5) pH; (6) sediment, by volume in a Lisenko volumetric cylinder in 5, 10, 15, 30, 60 and 120 min; (7) relative stability, by discolouration of methylene blue; (8) suspended matter with subdivision into volatile (at 900-1000°C) and nonvolatile parts; (9) dry residue, with division into volatile and non-volatile parts; (10) 5-day BOD and total BOD; (11) total acidity and alkalinity of water when titrated with various indicators; (12) partial oxygen demand (by  $\text{KMnO}_4$ ); (13) chemical oxygen demand (COD).

Each sample of industrial sewage is also tested for the presence of specific pollutants: iron, copper, chromium, cobalt, nickel, zinc, cadmium, mercury, sulphates, sulphites, cyanides, phenols, formaldehyde, synthetic surface active substances, etc.

Many of these substances are determined in the same way as in the analysis of natural waters, for example, dry residue, pH, total and partial oxygen demands, clarity, 5-day BOD, etc. All these determinations have been described in detail in special literature and only some of them will be discussed in this book.

**Relative Stability of Sewage.** The relative stability of sewage is the ratio of oxygen in water (dissolved oxygen, nitrite and nitrate oxygen) to the total BOD of the effluent. The relative stability is

expressed in per cent. The relative stability can be measured by the time required to consume all the oxygen contained in the water in the presence of methylene blue as an indicator.

Before testing a sample of sewage for stability, free acid or alkali is neutralized against bromothymol blue and other bactericides are removed. Next, microflora of the sewage is added to the sample. The sample is transferred into a 150-ml volumetric flask, 0.4 ml of methylene blue (0.5 g per litre of solution) is added, the liquid is mixed thoroughly, sewage is added to the mark and the flask is covered with a glass cap provided with a hydraulic seal. The contents are stirred again and the flask is placed in a thermostat where it is kept at a temperature of 20°C.

*The number of days which have passed till the moment when the liquid is discoloured is the time when the sample begins to rot.*

The relative stability of sewage at 20°C can be calculated using this formula

$$S = (1 - 0.794^{\tau})100$$

where  $S$  is the relative stability of sewage, in per cent;  $\tau$  is the number of days during which all oxygen is consumed (the time when the sample begins to decay).

Table 10.1 gives the terms (calculated with the above formula) of sewage stability depending on the length of standing (in days) at a temperature of 20°C.

Table 10.1

Relative Stability of Sewage Depending on  
Time of Discolouration of Methylene Blue

Time of discoloura- tion, days	Stability, per cent	Time of discoloura- tion, days	Stability, per cent	Time of discoloura- tion, days	Stability, per cent
0.5	11	6.0	75	12.0	94
1.0	21	7.0	80	13.0	96
2.0	37	8.0	84	14.0	97
3.0	50	9.0	87	16.0	97
4.0	60	10.0	90	18.0	98
5.0	68	11.0	92	20.0	99

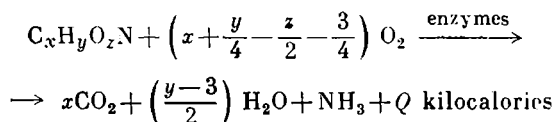
Table 10.1 shows that even the most perfect biological purification fails to remove all oxygen consuming wastes. Hence, biochemical methods cannot completely purify sewage and it will always contain residual quantities of organic matter.

If the quantity of dissolved and bound (nitrites, nitrates, BOD) oxygen is known, the stability should not be measured to control the operation of the plant.

**BOD of Sewage.** A 5-day and total BOD are distinguished. *These are the amounts of oxygen (mg/litre) spent for biochemical processes*

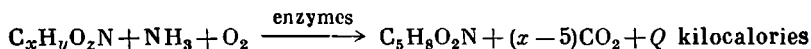
during five days, and the quantity of oxygen (mg/litre) spent by the biochemical processes till the reaction of nitrification begins, respectively.

As has already been said, the biochemical processes are connected with metabolism of microorganisms which consume oxygen to work out the energy necessary to maintain the vital processes and the synthesis of cell material. Schematically, these processes can be expressed by equations, provided the total ratio of the vitally important elements which are part of all organic compounds contained in the sewage are expressed as a compound with the simplest formula of  $C_xH_yO_zN$ . The oxygen demand for respiration will then be



The factors at the oxygen indicate the following:  $x$  means that one molecule of oxygen is spent for one carbon atom;  $y$  means that  $1/4$ th oxygen molecule is spent for one hydrogen atom; the bound oxygen is not included into the BOD (it is subtracted); each atom is  $1/2$  of the oxygen molecule ( $z/2$ ); nitrogen is reduced to ammonia with the consumption of three hydrogen atoms which corresponds to the decrease in the oxygen quantity by  $3/4$ th of a molecule.

The following (tentative) process occurs during synthesis of cell substances:



where  $C_5H_8O_2N$  is the mean ratio of the main elements in the cell substance of bacteria.

The total quantity of oxygen spent in these processes corresponds to the total BOD.

BOD is determined by several methods.

1. The standard dilution method is used to characterize strongly polluted waters and their BOD.

2. The method for determining the total BOD of industrial sewage which difficultly undergo biochemical oxidation.

3. The method for determining BOD by blowing oxygen is intended to analyze strongly polluted surface natural waters with low oxygen concentration.

The first and the second methods require special preliminary treatment of samples.

The procedure is as follows. A specially pretreated water is placed in several bottles provided with ground-in stoppers. The glass bottles are filled so that air bubbles are not formed. Dissolved oxygen is determined in one or two bottles immediately, while in the others it is determined after incubation for a certain time. The bottles are

kept in a thermostat at a temperature of 20°C in the dark. BOD is determined by the difference of oxygen content in the sample before and after incubation. If the sample was diluted, this should be taken into account. The results of the determinations are expressed in milligrams per litre of water. The test period should preferably be indicated (in days); if not specified, BOD indicates the consumption of oxygen during a five-day incubation.

Samples of water with high 5-day BOD should be diluted with special water containing inorganic nutrients in amounts sufficient for normal aerobic processes. (The diluting solution is prepared from distilled water.) If the sample does not contain saprophytic microflora, it is added to the diluting solution with small doses of public sewage (1 mg per litre), or river water (from 10 to 50 ml per litre).

The sample should be prepared so that before incubation it contained about 8.8 mg/litre of oxygen (at 20°C), while in five days the oxygen content should be not less than 3 mg/litre.

The degree of dilution of the sample should agree with the value of a 5-day BOD (see Table 10.2).

Table 10.2

Recommended Dilution of Water Samples for Determining BOD

Dilution	Sample volume in one litre of mixture, ml	Range of BOD levels, mg/litre O <sub>2</sub>	Dilution	Sample volume in one litre of mixture, ml	Range of BOD levels, mg/litre O <sub>2</sub>
1	1000	0-6	0.02	20	100-300
0.5	500	4-12	0.01	10	200-600
0.2	200	10-30	0.005	5	400-1200
0.1	100	20-60	0.002	2	1000-3000
0.05	50	40-120	0.001	1	2000-6000

**Determining Velocity Constant of the Total BOD.** Biochemical oxygen demand (BOD) of municipal sewage obeys the law of the first order reactions,  $v = kc$ , where  $v$  is the velocity of the reaction,  $c$  is the concentration of the reactant,  $k$  is the proportionality factor or the velocity constant of a chemical reaction. The kinetic equation of the first order reaction has the following form

$$k = \frac{1}{\tau} \ln \frac{a_0}{a_0 - x}$$

where  $k$  is the velocity constant of the chemical reaction;  $a_0$  is the initial concentration of the substance, mole/litre;  $x$  is the concentration of the substance which has reacted by the moment of time  $\tau$ , mole/litre,  $(a_0 - x)$  is the concentration of the remaining substance by the moment of time  $\tau$ , mole/litre; and  $\tau$  is the time, in days.

This equation can be rearranged so that its left part is only the ratio of the concentrations:

$$\ln \frac{a_0}{a_0 - x} = -k\tau$$

The equation shows that equal doses of the starting substance will react in equal lapses of time. Let us calculate what amount, out of the initial 100 g, will decompose each day, in the course of five days, provided 15 per cent of its initial amount are converted during the first day:

Initial amount of substance, g	Time, days	Quantity of the mineralized substance, g
100.00	1	15.00
85.00	2	12.75
72.25	3	10.84
61.41	4	9.21
52.20	5	7.83
Residue 44.37		55.63

*Determining BOD in Successive Samples.* According to this method, BOD is determined at intervals of 2 and 4 days or 3 and 6 days. To that end, dissolved oxygen is determined in the sample prepared for determining BOD and then at specified intervals after sample canning. BOD for both terms are determined and the velocity constant  $k$  for the biochemical process is determined:

$$k = \frac{1}{\tau} \ln \frac{\text{BOD}_{2\tau}}{\text{BOD}_{2\tau} - \text{BOD}_{\tau}}$$

Then the total BOD is determined (with conversion of the natural logarithm into decimal):

$$\text{total BOD} = \frac{\text{BOD}_{\tau}}{1 - 10^{-k\tau}}$$

The velocity constant  $k$  of biochemical oxygen demand depends on the temperature, the mass of microorganisms (mineralizers), on their ability to oxidize substances contained in the given medium.

Below is given the calculation of the velocity constant for mineralization of municipal sewage at 20°C.

Length of process, days	1	2	3	4	5
Residual substance, in per cent of initial ( $a - x$ )	79.5	63.4	50.0	40.0	31.7
Mineralized substance ( $x$ )	20.5	36.6	50.0	60.0	68.3

Let us calculate  $k$  for the first five days (using the experimental data):

$$k = \frac{1}{\tau} \ln \frac{100}{100 - x_1}$$

$$k_1 = \frac{2.3}{1} \log \frac{100}{100 - 20.5} = \frac{2.3}{1} \log \frac{100}{79.5} = 0.2300$$

$$k_2 = \frac{2.3}{2} \log \frac{100}{100-36.6} = \frac{2.3}{2} \log \frac{100}{63.4} = 0.2252$$

$$k_3 = \frac{2.3}{3} \log \frac{100}{100-50} = \frac{2.3}{3} \log \frac{100}{50} = 0.2307$$

$$k_4 = \frac{2.3}{4} \log \frac{100}{100-60} = \frac{2.3}{4} \log \frac{100}{40} = 0.2288$$

$$k_5 = \frac{2.3}{5} \log \frac{100}{100-68.3} = \frac{2.3}{5} \log \frac{100}{31.7} = 0.2292$$

The mean value of  $k$  is 0.2288.

The concentration of organic matter in sewage (determined by BOD) changes with time. But it should be noted that this process does not obey the kinetic law of the first order reaction during the entire process of mineralization of organic substances and therefore it is used to characterize the process only to a limited extent. It is assumed that the time required for complete oxidation of oxygen-demanding wastes is equal to the time during which the process is completed by 99 per cent ( $\text{BOD}_\tau = 0.99\text{BOD}_{\text{total}}$ ) Then

$$\tau = \frac{1}{k} \log \frac{\text{BOD}_{\text{total}}}{\text{BOD}_{\text{total}} - 0.99\text{BOD}_{\text{total}}}$$

It follows from the equation that the time of mineralization of organic matter depends on the velocity constant of this process. If  $k$  is 0.05, the organic matter will all be mineralized in 40 days, if  $k$  is 0.1, in 20 days, and if  $k$  is 2.5, in 8 days.

The velocity constant for municipal sewage varies from 0.15 to 0.25 day<sup>-1</sup> at a temperature of 20°C.

The nature of organic substance is very important for the velocity constant of the biochemical process. Therefore, the proportionality factor for industrial sewage containing various organic substances varies within wide limits. But one can select from the variety of values of  $k$  a certain mean value for a given type of sewage which will well agree with the experimental data obtained in the course of the oxygen consumption process.

The concentration of organic matter in industrial sewage is characterized by the total BOD determined by the magnitude of the velocity constant of the biochemical process  $k$  which changes with temperature. The dependence of the velocity constant of the oxygen consumption process  $k_{t_2}$  on the temperature of sewage (for the range of temperatures from 10 to 30°C) is expressed by the formula

$$k_{t_2} = k_{t_1} 1.047^{(t_2 - t_1)}$$

where  $k_{t_2}$  is the velocity constant at high temperature  $t_2$ ,  $k_{t_1}$  is the velocity constant at low temperature  $t_1$ .

Some industrial sewage does not consume oxygen during the first days since  $k_t = 0$ , but later it becomes energetic with  $k_t \geq 0.1$ .

This is so because the microflora of the medium is not adapted to a given pollutant. To avoid this, microflora adapted to the given sewage should be added to the dilution water.

BOD is determined in the laboratory at 20°C. To recalculate this value for another temperature, one should use the following formula:

$$\text{BOD}_{\text{total}(t)} = \text{BOD}_{\text{total } 20^{\circ}\text{C}} (0.02t + 0.6)$$

where  $t$  is the temperature of the sewage.

This formula agrees well with the experimental data for BOD of municipal sewage and some industrial waste waters. For example, for sewage containing petroleum products the total BOD at 30°C is higher than at 20°C.

**Chemical Oxygen Demand (COD).** The chemical oxygen demand is the quantity of oxygen required for complete oxidation of all reducing substances (of organic and inorganic origin) present in the water. COD of a given sample of water is determined by combustion of impurities with strong oxidants (potassium dichromate or potassium iodate) in an acid medium. All elements are oxidized in these conditions: carbon is oxidized to  $\text{CO}_2$ , sulphur to  $\text{SO}_3$ , phosphorus to  $\text{P}_2\text{O}_5$ , hydrogen to  $\text{H}_2\text{O}$ ; only oxygen spent for oxidation of ammonia is not accounted because the formation of nitrites and nitrates is not included into COD.

If only organic matter is contained in sewage and the amounts of the pollutants and their composition are known, COD can be determined by stoichiometric equations. COD is mainly used to characterize industrial effluents containing organic matter. COD is always higher than  $\text{BOD}_{\text{total}}$  (Table 10.3) because not all pollutants are mineralized in biochemical processes and the metabolites of cell

Table 10.3

Relationships between  $\text{BOD}_{\text{total}}$  and COD (after Bazyakina)

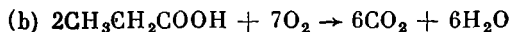
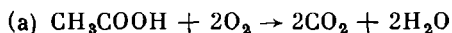
Pollutant	Formula	Amount per gram of substance		BOD in per cent of COD
		COD	$\text{BOD}_{\text{total}}$	
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	2080	1820	87.4
Acetone	$\text{CH}_3\text{COCH}_3$	2170	1680	76.5
Acetic acid	$\text{CH}_3\text{COOH}$	1070	860	80.0
Phenol	$\text{C}_6\text{H}_5\text{OH}$	2380	1100	46.0
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6$	1010	600	59.5

microorganisms, which are not mineralized by incubation, are returned into the medium.

COD of industrial effluents can be calculated if the composition of the organic pollutants is known.

Let us, for example, determine COD of sewage containing 1 g of acetic acid and 1 g of propionic acid in one litre.

*Solution:* (1) Write the equation for combustion of the acids:



(2) Determine the required quantity of oxygen to burn the acids:

- (a) for combustion of 60 g of  $\text{CH}_3\text{COOH}$  64 g of  $\text{O}_2$  are required;  
 for combustion of 1 g of  $\text{CH}_3\text{COOH}$   $x_1$  g of  $\text{O}_2$  are required;  $x_1 = 1.0666$  g  
 (b) for combustion of 74 g of  $\text{CH}_3\text{CH}_2\text{COOH}$  112 g of  $\text{O}_2$  are required;  
 for combustion of 1 g of  $\text{CH}_3\text{CH}_2\text{COOH}$   $x_2$  g of  $\text{O}_2$  are required;  $x_2 = 1.5135$  g

$$\text{COD}_{\text{total}} = 1066.6 + 1513.5 = 2580.1 \text{ mg/litre}$$

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### 10.3. Protection of Surface Waters from Pollution with Sewage (Ministry of Land Reclamation and Water Management of the USSR. Moscow, 1974)

In compliance with the "Rules of Protection of Surface Waters from Pollution with Sewage" sewage should be withdrawn from the point where it is formed. The object of the present Rules is to preclude pollution of water bodies, such as rivers, springs, large water reservoirs, lakes, ponds, and artificial canals used for water supply and fish-raising.

The criterion for the pollution of water is the deterioration of its organoleptic properties and the appearance of substances noxious to man, animals, birds, fish, and organisms used in the manufacture of fodder, as well as the increased temperature of water which changes the conditions for normal aquatic life.

The conditions of sewage disposal into water bodies should be agreed upon with the authorities responsible for the control and protection of waters, and also with sanitary and epidemiological services responsible for the protection of aquatic life (fish).

Those who violate the "Rules" should be persecuted by the law or bear administrative responsibility.

When sewage is discharged into water bodies, its composition and amount should be considered, along with proper consideration of the industrial and social importance of a given water body, its character and capacity.

**General Requirements for Composition and Properties of Water Used for Domestic and Social Purposes**

Composition and properties of water	Purpose	
	for centralized and autonomous water supply systems and also for use in public catering establishments	for bathing, sports and recreation of population, and also open water bodies inside settlements
Suspended matter	<p>The amount of suspended matter should not increase by more than</p> <p>0.25 mg/litre   0.75 mg/litre</p> <p>The amount of suspended matter in water of open bodies (containing over 30 mg/litre of natural mineral substances) may increase, in normal level periods, by 5 per cent</p> <p>Suspensions, settling at rates exceeding 0.4 mm/sec and 0.2 mm/sec, shall not be discharged into running and standing water bodies respectively</p>	
Floating impurities	No films, spots of mineral oils or accumulation of other impurities are allowed to float on the surfaces of water bodies	
Odour and taste	<p>Water should not have odour or smack that can be assessed by more than 2 degrees in</p> <p>untreated water or chlorinated water   untreated water</p>	
Colour	<p>Water should not give its odour or taste to fish</p> <p>Colour of water should not be perceived in</p> <p>20 cm high column   10 cm high column</p>	
Temperature	The temperature of water in summer should not rise, due to the disposal of sewage, more than 3°C over the mean monthly temperature of water in the hottest month during past ten years	
pH	This should be within the range 6.5-8.5	
Mineral composition	The dry residue should not exceed 1000 mg/litre; the figure includes 350 mg/litre of chlorides and 500 mg/litre of sulphates	To agree with requirements of "Taste", (q. v.)
Dissolved oxygen	Not less than 4 mg/litre in any season in a sample taken before noon (12 a. m.)	
BOD	<p>The complete oxygen demand of water at 20°C should not exceed</p> <p>3.0 mg/litre   6.0 mg/litre</p>	

*Continued*

Composition and properties of water	Purpose	
	for centralized and autonomous water supply systems and also for use in public catering establishments	for bathing, sports and recreation of population, and also open water bodies inside settlements
Pathogenic causative agents	Water should be free from pathogenic agents. Sewage which may contain pathogenic causative agents should be disinfected after preliminary treatment. Biologically treated municipal sewage is disinfected to coli-index not over 1000 in one litre, residual chlorine content being not less than 1.5 mg/litre. The methods of disinfection and preliminary treatment (mechanical or biological) should be agreed upon with State Sanitary Inspection in each particular case.	
Poisons	These should not be contained in concentrations which can produce direct or indirect harm to man	

## 10.4. Treatment of Sewage

The sanitary requirements for the composition and properties of water bodies appreciably limit the discharge of sewage into water bodies. The sewage should be specially treated before disposal. The methods of sewage treatment fall into two groups, mainly, destructive and regenerative methods.

The *destructive methods* destroy the pollutants by oxidation or reduction. The products of decomposition formed (gases or precipitates) are then separated from the water or they may remain in solution form. The methods comprise biological treatment on artificial units, known as aeration tanks, on aeration filters, filtration beds, etc. The methods also include chemical treatment.

The destructive treatment requires the use of possibly cheap methods to cut the cost of treatment.

The *regenerative methods* are used to recover valuable substances that may be contained in sewage. For example, the sewage of producer gas units contains considerable amounts of phenol, acetic acid, which are recovered by the regenerative methods in the free state and can be reused. Hence two objects are achieved, namely, the purification of water and the utilization of valuable wastes.

The regenerative treatment can only be used in cases where the cost of the recovered product is higher than the cost of the recovery

process. The regenerative methods often do not purify water to the state when it can be discharged into water bodies. Such waters then undergo destructive treatment.

The selection of a particular method of treating sewage depends on the composition and properties of the sewage, and also on the character and the capacity of the water body, its economical importance and special uses. All these considerations can be used to decide whether or not a particular sewage should be treated at all, and if it should be treated, then to what degree of purity.

Biological treatment is necessary if organic matter is to be removed from water. If impurities are of inorganic origin, biological treatment is not reasonable.

The following procedures are involved in the treatment of sewage: (1) removal of coarse particles by settling and coagulation; (2) extraction of pollutants; (3) adsorption of pollutants; (4) distillation of pollutants with steam; (5) neutralization of acids and bases; (6) flotation of pollutants; (7) chlorination of water; (8) chemical treatment; (9) crystallization; (10) biological treatment; (11) fermentation of the sludge in anaerobic conditions.

Water quality is controlled at each stage of its treatment at the water treatment plant so that the process could be properly adjusted and the operation of separate units of the plant could be assessed.

**Removal of Suspended Matter\*.** Various substances can be suspended in water. Light particles float to the surface and heavy settle on the bottom.

Settling is effected in horizontal, radial, and vertical settling tanks, while oils and petroleum are retained in special oil traps.

When a water treatment plant is planned, and settling tanks and oil traps are designed, samples of water are analyzed in the laboratory to determine the kinetics of precipitation or floating of the suspended matter. The obtained data are used to determine the time for which the water should be settled to separate from coarse particles. If the settling process is slow, coagulation is used. The coagulant dose\*\* is determined experimentally along with pH of water and the kinetics of precipitation.

Salts of iron, aluminium, activated silica and polyacrylamide are used as coagulants. Spent potassium solutions containing magnesium chloride and magnesium sulphate, and substances having adsorbing properties, such as clay, ash, humins, coal, ferrochromium slags, can also be used for the purpose. Ferrochromium slags are suitable

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\* Suspended matter are substances which are retained on a dry ashless filter and dried at a temperature of 105-110°C to constant weight. The content of suspended matter in water is expressed in mg/litre.

\*\* The coagulant doses for industrial waters vary within a wide range, from 100 to 500 mg/litre and over.

for coagulation of acid sewage since they both neutralize and separate the sewage from suspended matter.

Activated silicic acid is used together with aluminium or iron coagulant. This decreases the consumption of coagulants and promotes formation of dense and quickly flocculating precipitates.

Activated silicic acid solution is prepared from equimolecular quantities of dilute solution of soluble glass,  $\text{Na}_2\text{SiO}_3$ , and ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , with subsequent dilution to 2 per cent  $\text{SiO}_2$  content. In an hour of ageing, the  $\text{SiO}_2$  content is further reduced to 1.3 per cent and below by dilution. The following sequence should be observed while adding the coagulants: iron or aluminium coagulants should be added only after the sol of silica has been distributed in the water.

Sewage can sometimes be coagulated by changing the pH of water. For example, municipal sewage contains proteins which, due to their amphoteric properties, can precipitate in the isoelectric state at pH from 4 to 7. Soaps and sparingly soluble free high-molecular fatty acids are also precipitated by acidification.

**Extraction.** The separation of pollutants from water with some other liquid is called *solvent extraction*. A liquid, which is immiscible with water, is selected for extraction of pollutants which are better dissolved in this liquid than in water.

Organic liquids, such as benzene, mineral oils, carbon tetrachloride, carbon disulphide and others are used as extracting agents. Solvent extraction is effected in apparatuses known as *extractors*. Extraction can be a batch or continuous process. (Batch process is used to purify small quantities of sewage.) The diagram of a continuous extraction plant is shown in Fig. 10.1.

An extractor is a packed column into which water and the extracting agent are delivered. If the extracting agent is lighter than water, it is fed in an upstream flow as shown in Fig. 10.1. If otherwise, the extracting agent is fed at the top of the column. In order to maintain constant level, water is drained from the column through a syphon communicated with its upper part. When the extracting agent has been saturated, it is delivered to the settling tank, where the liquids separate.

If sewage contains several components, selective solvents are used to extract each particular pollutant from the water. For example, in order to extract phenol from its mixture with fatty acids, tricresyl phosphate is used as a selective solvent. (The concept

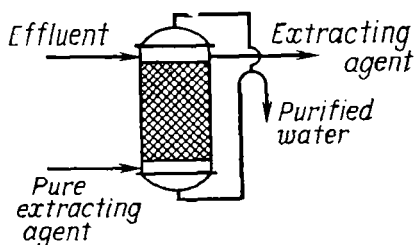


Fig. 10.1. Continuous extraction unit

“selective” refers only to this particular system). The disadvantages of this method are solubility of the extracting agent in water and incomplete destruction of emulsion.

The necessary quantity of the extracted substance is determined experimentally in each particular case. To that end, a sewage sample is divided into equal portions and each is treated with equal amounts of various extracting agents. The residual quantity of the pollutant is then determined in each extracted portion of sewage. The experiments are carried out in various media (acid and alkaline). As soon as an effective extracting agent has been found, the conditions for emulsification and the velocity of emulsion separation are determined and the distribution coefficient of the pollutant between the extracting agent and water is established. To that end, the sewage is treated several times with equal volumes of the solvent and the component in question is determined after each operation. The distribution coefficient is then determined by the formula

$$K = \frac{c_{\text{H}_2\text{O}}}{c_{\text{extr}}}$$

where  $K$  is the distribution coefficient;  $c_{\text{extr}}$  is the equilibrium concentration of the solute in the solvent; and  $c_{\text{H}_2\text{O}}$  is the equilibrium concentration of the solute in water.

**Adsorption.** This treatment of sewage consists in adsorption of the dissolved substances on the surfaces of the adsorbent. Static and dynamic adsorption are distinguished. Dynamic adsorption occurs on the surfaces of the adsorbent when sewage passes the filter packed with the adsorbent, while adsorption in static conditions consists in adding certain amounts of the adsorbent to a given amount of water. During static adsorption, the concentration of the solute decreases to equilibrium, while in dynamic adsorption process, the concentration of the solute decreases gradually as the water passes through the adsorbent bed. If the depth of the filtering bed is sufficiently great, practically all solute can be removed from the solution. If the adsorbent is a cheap material (peat, saw dust, slags, etc.) it can be discarded together with the adsorbed substance. But if the pollutant and the adsorbent are of certain value, the adsorbent is regenerated by distillation of the adsorbed material, its extraction with a suitable solvent, or by converting the adsorbed substance into a difficultly soluble derivative. It is often impossible to regenerate the adsorbent completely because part of it reacts chemically with the adsorbed substance.

**Steam Distillation.** Many organic compounds are decomposed with heating to temperatures below their boiling point. In such cases it is impossible to obtain a pure substance by distillation at atmospheric pressure. If a substance in question is readily soluble in water, it can be distilled under reduced pressure which is so

selected that the liquid should boil at a temperature below the point at which the substance decomposes. If the substance is insoluble in water, it should be distilled with steam. The mixture will boil at a temperature below 100°C under atmospheric pressure. The

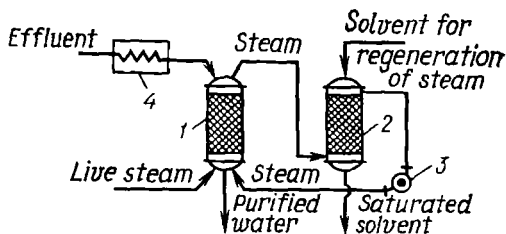


Fig. 10.2. Evaporation column

composition of the vapour does not depend on the overall composition of the liquid since mole fractions of the components in steam ( $1 - y$ ) and ( $y$ ) are related as constants at a given temperature,  $p_1$  and  $p_2$ :

$$1 - y = \frac{p_1}{p_1 + p_2}; \quad y = \frac{p_2}{p_1 + p_2}$$

Hence a low-volatile liquid can vaporize at a temperature below its boiling point, by boiling with another liquid, which is more volatile, immiscible with it, and chemically inactive toward it. In order to raise the yield of the process, superheated steam is used which increases the temperature of the distilled substance to increase the pressure of its saturated vapour and its mole fraction in the distilled mixture.

**Example.** Consider steam distillation of myristic acid ( $C_{13}H_{27}COOH$ ). The saturated vapour pressure of this acid at 200°C is 14.5 mm Hg. When superheated steam (at 200°C and 740 mm Hg) is passed through the acid, a mixture of vapours of both substances is obtained. The mole fractions of steam ( $1 - y$ ) and of the acid ( $y$ ) are

$$\{(1 - y) = \frac{(740 - 14.5)}{740} = 0.980; \quad y = \frac{14.5}{740} = 0.020$$

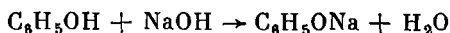
The components are contained in the condensate in the following quantities (per mole of the vapour mixture):

$$\begin{array}{ll} \text{Water} & \omega_1 = (1 - y) M_1 = 0.980 \times 18 = 16.64 \text{ g} \\ \text{Acid} & \omega_2 = y M_2 = 0.020 \times 228 = 4.56 \text{ g} \end{array}$$

The quantity of water required to distil 1 kg of the acid is  $\frac{16.64}{4.56} = 3.65 \text{ kg}$  (with steam superheated to 200°C).

The distillation can be effected on batch or continuous distillation columns. A schematic diagram of a column for steam distillation is shown in Fig. 10.2. As sewage flows down the packing in the column to meet the uprising live steam it heats to 100°C. Volatile pollutants pass into vapour phase and are removed together with steam. The vapours pass from the evaporation column 1 into the adsorption column 2 where the substances entrapped with steam are separated. For example, phenol is separated from steam by passing it through a solution of alkali heated to 100°C. The alkali

converts phenol into the phenolate  $C_6H_5ONa$  which is non-volatile with steam:



Fan 3 returns dead steam to the evaporation column to complete the cycle.

**Neutralization of Acids and Bases.** The Regulations prohibit the discharge of acid and alkaline sewage into water bodies because it kills the aquatic life. Before disposal, such sewage should be neutralized. Only the concentrations of free acids or alkalies are taken into account when neutralization plants are designed.

Sewage is neutralized by adding the corresponding reagent or by filtration through neutralizing materials. Sewage is passed through filters packed with lime, limestone marble, dolomite, and calcined dolomite. Alkaline waters are neutralized by commercial sulphuric acid. Sewage is passed through tanks into which reagents are added in the form of milk of lime, thick paste, or dry powder. The dose of lime should be calculated by the acidity of the sewage.

**Example.** The acidity of sewage is 12 mg-equiv/litre. Ten cubic metres of sewage should be neutralized. What quantity of lime is required?

**Solution.** One litre of the sewage contains 12 mg-equiv of the acid, and one cubic metre, 12 g-equivalents.

1 g-equiv of  $CaO$  is 28 g

$$x = 12 \times 28 = 336 \text{ g}$$

12 g-equiv of  $CaO$  are  $x$  g

To neutralize one cubic metre of the sewage, 336 g of  $CaO$  are required, and to neutralize 10 cubic metres, 3.36 kg of  $CaO$ .

The natural neutralizing capacity of a water body should be considered when neutralizing sewage, and only that part of the acid which cannot be neutralized naturally should be neutralized artificially.

The quantity of sewage that can be discharged into a water body should be calculated by the following procedure. Let the alkalinity of a water body be  $a$  mg-equiv/litre, while the acidity of the sewage in question,  $b$  mg-equiv/litre. Then, to neutralize the sewage, it should be diluted in the water body minimum  $b/a$  times. If the dilution is weaker, part of the sewage should be neutralized artificially.

Sewage is neutralized by passing it through mutation filters packed with chalk, marble, dolomite or calcined dolomite (the composition  $xCaCO_3 \cdot yMgCO_3 \cdot zCaO \cdot pMgO$ ).

Calcined dolomite is the most suitable filtering aid, and its most important constituent is magnesia which has some advantages over carbonates and calcium oxide: (a) magnesia is insoluble in water and does not pass into solution in the absence of acids; (b) when

strong acids are neutralized by magnesia, carbon dioxide is not formed and hence carbonate hardness does not increase in neutralized water; (c) the velocity of neutralization with magnesia is higher than with carbonates.

Moreover, when strong acids are neutralized by mutation filtration through calcined dolomite, it is not necessary to increase the height of the filter to bind  $\text{CO}_2$  and filters of normal size can therefore be used. This packing reacts with all strong and weak acids and does not give precipitates on the filter.

Mutual neutralization of sewage should also be considered. If acid and alkaline sewage should be discharged, it is reasonable to neutralize them by mixing. The residual free acid or alkali in thus neutralized sewage should be determined analytically.

For example, the acidity of sewage in question is  $a$ , the daily amount of the sewage is  $m$  cu.m.; the basicity of alkaline sewage is  $b$  and its daily amount is  $n$  cu.m. The sewage is neutralized completely if  $am = bn$ . If, however,  $am$  is greater than  $bn$ , the mixed sewage reacts acid, and if otherwise, it reacts alkaline. Excess acidity or alkalinity is then neutralized by any suitable method.

**Flotation.** Valuable impurities are recovered from sewage by *flotation*. The method is based on different wettability of hydrophobic and hydrophilic particles. The *froth-flotation procedure* consists in blowing air through sewage. Particles of hydrophobic valuable impurities are adsorbed on the surfaces of the rising air bubbles to float on the surface of the liquid.

In order to increase the flotation effect, surface active substances are added to water (Matsnev, 1965). These substances, such as petroleum, masouts, resins, kerosene, high-molecular fatty acids, mercaptans, xanthogenates, etc., decrease the surface tension of the liquid to weaken the bonds between water and the solid.

The flotation process can be intensified by adding *foaming agents* (heavy pyridine, creosol, phenols, synthetic detergents) which also decrease the surface tension of the liquid and increase the dispersion and stability of air bubbles.

Substances increasing surface tension in liquids (mineral acids, bases, salts) inhibit flotation.

Flotation units are widely used in pulp-and-paper industry to recover fine fibres from the screened sewage. They are used in the manufacture of adhesives, in oil refinery, at slaughter houses to trap fat from water.

**Chlorination.** Chlorine and its compounds are used to treat both municipal and industrial sewage. Chlorine kills pathogenic microorganisms, unpleasant odour (e.g. of hydrogen sulphide and other sulphur compounds), and algae growing in cooling water.

Chlorine quenches foam in fat- and oil-traps by destroying colloidal systems. It is used to fight larvae of flies on biological

filters; and its ability to react with other substances is used to remove poisons, e.g. cyan, from sewage.

Liquid chlorine from steel cylinders is used for chlorination. Chlorine is passed either directly into the liquid, or is first dissolved in water and then added as chlorine water.

Chloride of lime is used to treat small bulks of sewage. It contains 25-35 per cent active chlorine and is also used to coagulate colloidal substances in sewage (calcium hydroxide is formed).

Chlorine dioxide,  $\text{ClO}_2$ , is used to remove unpleasant odour from sewage, discharged from plants manufacturing fish flour and from slaughter houses. It is also used to decontaminate cyan-containing sewage from metal-plating shops. But the high cost of chlorine dioxide prevents its wide use.

Doses of the reagent are calculated by the active chlorine content. The degree of required purification and the reactivity of sewage are also taken into account. In each particular case, the chlorine dose and the time of its contact with water are determined experimentally. Residual concentrations up to 0.5 mg/litre of active chlorine quickly vanish when the treated sewage is discharged into an open water body to bring no harm to fish or aquatic plants. The only condition is the absence of phenols in the water body, since it can form chlorophenol with chlorine. Even insignificant amounts of chlorophenol give an unpleasant "chemical" odour to water and the biota.

**Chemical Treatment of Sewage.** This consists in treatment with chemical reagents to separate impurities in the form of a precipitate or gas.

For example, sewage containing salts of hexavalent chromium are treated with sodium hydrosulphite,  $\text{NaHSO}_3$ , sodium sulphite,  $\text{Na}_2\text{SO}_3$ , or ferrous sulphate,  $\text{FeSO}_4$ , in an alkaline medium with subsequent removal of precipitated chromium hydroxide,  $\text{Cr}(\text{OH})_3$ .

The oxidation of phenols and other organic substances with atmospheric oxygen in the presence of a catalyst can also be regarded as chemical purification of sewage.

When industrial sewage is treated, chemical precipitation is used either as an independent method or as a preliminary stage before biological purification. Chemical additives decolourize water, clarify it, and precipitate sludge.

**Crystallization.** Concentrated industrial sewage can be purified by crystallization. As a rule, crystals precipitate from saturated solutions. This is effected by evaporation of liquids with subsequent lowering of temperature.

Crystallization is carried out in special apparatus, e.g. in evaporators working under atmospheric pressure or in vacuum with heating, or in batch apparatus with natural cooling by the vaporizing water, etc.

The crystal hydrate method of demineralization of water has

a great practical importance in the treatment of industrial sewage, which is separated by this method into brine and water. The method consists in contacting any aqueous solution with a hydrate-forming agent M (propane, chlorine, Freons,  $\text{CO}_2$  and others) which extracts water from the system to form a solid crystalline substance, the crystal hydrate, having the formula  $\text{M} \cdot n\text{H}_2\text{O}$ . Pure water molecules are a part of the crystalline structure of the hydrate-forming substance. Crystal hydrates look like thawed snow. By proper selection of a hydrate-forming agent, it is possible to obtain crystal hydrates at temperatures from 8 to  $25^\circ\text{C}$  and a pressure from 1 to 6 atm (Meltser, Smirnov *et al.*, 1973).

The precipitated crystal hydrates are separated from the brine, washed to remove the brine film from the crystals, and then melted to obtain pure water and the hydrate-forming agent, which is reused in the process. The method can be used to concentrate sewage in order to separate valuable products from it.

**Biological Treatment of Sewage.** The method consists in the decomposition of finely dispersed matter, colloidal and dissolved substances by metabolism of aerobic microorganisms.

Biological treatment depends on the following factors: (a) the susceptibility of organic substances contained in sewage to biochemical oxidation; (b) the presence of the necessary nutrients, such as nitrogen, phosphorus, potassium, carbon, vitamins and microelements; (c) concentration of pollutants should not exceed the specified limits; (d) the pH of the medium should be close to neutral; (e) the concentration of biologically toxic substances should not exceed the specified norm; (f) sewage should be free from surface active substances which interfere with normal contact of the liquid with oxygen of the air.

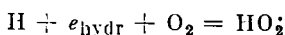
Normally, industrial sewage does not meet these requirements and requires special pretreatment.

**Fermentation of Sludge.** The sludge sedimented from sewage is fermented in anaerobic conditions in which organic substances are acted upon with various symbiotic organisms and pass through many intermediate stages before they decompose to carbon dioxide and methane. For more detail see Chapter 13.

**Radiation Treatment of Sewage.** This is intended to purify sewage from organic pollutants. The process is known as *radiolysis*, which consists in the conversion of dissolved substances by the absorbed energy of the ionizing radiation. The chemical changes occur due to the absorption of ionizing radiation. The result of this process is ionization and excitation of water molecules which lead to formation of chemically active particles, the radicals. In dilute solutions, which completely absorb ionizing radiation, these particles are hydrogen atoms, hydrated electrons  $e_{\text{hydr}}^*$ , and the radicals  $\text{OH}\cdot$ .

\* Active electrons in conditions of aqueous medium.

The active particles  $H$  and  $e_{\text{hydr}}$  are converted, in the presence of oxygen, into hydrogen peroxide radicals



The quantity of energy absorbed in the system is called the dose, which is expressed in rads or electron-volts. (A rad corresponds to the absorption of energy of 1 erg per cubic centimeter). The amount of energy absorbed in a system per second is called the dose strength and is expressed in rad/sec or eV/sec.

The radiation-chemical process is characterized by the yield of product  $G$ , i.e. by the quantity of the converted particles due to the absorption of 100 eV of the ionizing radiation energy.

The mechanism of the radiation treatment of industrial sewage depends on the concentration of the solute. For example, if the concentration of pollutants does not exceed  $1 \times 10^{-4}$  M, the radiation-chemical conversion of organic substances occurs through reactions by which the radicals  $H$ ,  $e_{\text{hydr}}$ ,  $OH\cdot$ ,  $HO_2\cdot$  and hydrogen peroxide  $H_2O_2$  are formed. Pollutants can enter chemical reactions of oxidation, reduction, combination, elimination of atoms or groups, etc. with these active particles.

The radical  $OH\cdot$  and hydrogen peroxide,  $H_2O_2$ , have oxidizing properties. The hydrogen atoms and hydrated electrons show these properties in an acid medium or in the presence of molecular oxygen. The hydrated electron in an acid medium (in the presence of hydrogen ion) forms atomic hydrogen:  $H^+ + e_{\text{hydr}} \rightarrow H$ , which can enter oxidation reactions of the type  $RH + H \rightarrow H_2 + R\cdot$ . In the presence of oxygen, the hydrogen atoms and hydrated electrons form hydrogen peroxide radicals,  $HO_2\cdot$ , having oxidizing properties.

It has been found experimentally that if an aqueous medium absorbs 100 eV of the ionizing energy, the following quantity of oxidizing equivalents arise: 2.8 for the radical  $OH\cdot$ , 0.6 for the hydrogen atom; 2.3 for the hydrated electron; and 0.8 for  $H_2O_2$  (since 0.4 molecule of  $H_2O_2$  is formed). The total number of oxidizing equivalents during radiolysis of water in the presence of oxygen is:

$$\begin{aligned} G_{OH} + G_H + G_{e_{\text{hydr}}} + G_{H_2O_2} &= 2.8 + 0.6 + 2.3 + 0.8 = \\ &= 6.5 \text{ equiv/100 eV} \end{aligned}$$

If we add the oxidizing equivalent of the hydrogen peroxide radical  $HO_2\cdot$  (which is 3), the summary yield of the oxydation will be  $G = 6.5 + 3 = 9.5$  equiv/100 eV. Tentative calculations show that this process can be used for the final treatment of water in which the concentration of pollutants varies from  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  M.

If the concentration of pollutants exceeds  $1 \times 10^{-3}$  M, the treatment becomes inefficient for economical considerations since it requires large amounts of radiation energy.

At the present time this method is used at many plants of biological treatment of sewage.

Tentative calculations show that, the other conditions being equal, the aerobic stabilization of activated sludge is more efficient than its anaerobic fermentation.

Sometimes the sludge is *conditioned* before mechanical dehydration. Coagulation with ferric chloride and lime is mostly used in this country.

High-molecular polyelectrolytes are used to condition sewage sludge in some countries. The reagent and its dose are selected experimentally. High-molecular compounds are highly effective to dehydrate sludge, their doses being hundreds of times smaller than of mineral coagulants.

Modern researchers condition sludge by freezing with subsequent thawing, by selecting suitable additives, electrocoagulation, radiolysis, etc.

*Thermal treatment* consists in keeping sewage sludge in autoclaves at a temperature of 170-200°C for 1-2 hours. This method disinfects the sludge and gives it the structure which improves its filtering properties and compression.

*Mechanical dehydration* is effected in vacuum filters, pressure filters, and centrifuges.

Vibration filtration can also be attributed to the mechanical method of dehydration. Vibration filtration ensures high productivity and is inexpensive.

For a more complete removal of moisture from the sludge, the mechanically treated sludge is given a thermal treatment in special apparatus.

A method has been offered to dry sludge in a fluidized bed into which the heat carrying medium is delivered at a temperature of 450-500°C. A small part of organic matter (up to 4 per cent) is burnt out from the dry sludge (residual moisture content, 6-10 per cent). Dry sludge is a gray granular material devoid of any specific odour.

The organic part of sewage sludge is *oxidized chemically in the liquid phase* by atmospheric oxygen at a temperature of 200-300°C. A sterile aqueous suspension of nonburnt substances and ash is formed as a result. This can be easily destroyed by settling and filtration.

Sewage sludge is used as fertilizer, as fortification of animal feeds, for recovery of valuable products; it is used also in the industry of building materials, as adsorbing materials in the treatment of sewage, etc. If the sludge isolated from sewage is practically useless it can be used as fuel.

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## CHAPTER ELEVEN

# MICROBIOLOGY OF DRINKING WATER AND SEWAGE

Microbiology is the branch of science treating of minutest (invisible to the naked eye) organisms known as microbes.

The group of microorganisms comprises bacteria, actinomycetes (filamentous microorganisms), chlorophyll-free plants such as fungi, chlorophyll-containing plants, such as algae, protozoa and ultra-microbes, the special class of organisms with simpler organization, invisible with the microscope.

The word microbiology derives from the Greek words *mikros*, small and *bios*, life.

Microbiology deals with the structure and life of microorganisms. It studies their role in conversions of organic and inorganic substances in nature. The decomposition of organic substances in natural conditions and in artificial apparatus occurs with the active participation of microorganisms using organic matter as food. Proteins, fats, and carbohydrates are valuable foods for them.

When studying the processes occurring at water treatment plants, it is impossible to ignore the activities of microbes which often are the main cause of destruction of organic pollutants.

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### II.1. Brief History of General Microbiology

Bacteria are the most ancient inhabitants of the Earth. The scientists suppose that the first bacteria were smaller than modern ones. "Fossil" bacteria (their impressions) were found, together with blue-green algae, in deposits of the Cambrian and Precambrian periods. As the time passed on, the organisms developed to give filamentous forms which, in turn, gave birth to fungi.

The blue-green algae could originate from chromobacteria.

First reports on the existence of microorganisms appeared late in the 17th century. These were the reports of the Dutch scientist Anton van Leeuwenhoek (1632-1723) who was the creator of the first microscope. It could enlarge objects 160 times. Leeuwenhoek examined the material scraped off from his teeth, a drop of stagnant

water, hay infusion, and other materials. What he saw he described in detail in his book "Mysteries of Nature".

So bacteria were first seen in the 17th century, but people had made practical use of microorganisms long before this remarkable discovery. The ancient people knew how to prepare sour milk, yeast dough, grape wine, etc.

The first period of development of the science of microbiology (18th and early 19th centuries) was limited to observations and descriptions of morphology of microorganisms.

The first deeper examination in microbiology was made by the Russian scientist L. S. Tsenkovsky (1822-1887) who discovered a gelatinous accumulation, *zooglea*, in microbes. Since zooglea are characteristic of algae, he attributed bacteria to the plant world.

The science of microbiology was further developed by Louis Pasteur (1822-1895) who studied physiology of microorganisms and the life of microbes in nature. Pasteur proved the microbiological nature of fermentation (alcoholic, acetic acid, lactic, etc.) which had been considered to be of chemical nature. Pasteur offered a method to fight harmful bacteria by heat treatment of liquids, which is still widely used nowadays. The process is known as *pasteurization*.

Pasteur studied some diseases of man and animals to find out that the causative agents of the diseases are various microbes. He proved that the disease can be prevented if an attenuated culture of a given causative agent is administered to man. The method is widely used in the world now, and it is called *vaccination*.

Pasteur was followed by Robert Koch, the German bacteriologist (1843-1910). He confirmed Pasteur's idea that infectious diseases are caused in man by various pathogenic microbes. He suggested methods to control these bacteria and was actually the founder of *disinfection*. He discovered the tubercle bacillus, the agents causing cholera, he began using solid nutrient media for microbiological investigations, and thus prepared pure cultures of microorganisms.

Further development of microbiology is associated with the names of many Russian scientists such as I. I. Mechnikov (1845-1916), N. F. Gamaleya (1859-1949), D. I. Ivanovsky (1864-1920), S. N. Vinogradsky (1856-1953), and V. L. Omelyansky (1867-1928).

Mechnikov's works were of special importance. He discovered protective properties of living bodies, *phagocytosis*, consisting in the inactivating of pathogenic microbes in the blood by the white bodies of the blood, leukocytes. Mechnikov revealed the immune properties of the body, i.e. insusceptibility to infectious diseases. He worked out the theory explaining premature ageing of the body under the action of poisons produced by microbes in the intestine during the digestion. Mechnikov suggested the use of lactic acid bacteria (*Lactobacillus bulgaricus*) as antagonists to these microbes.

They inhibit the growth of putrefactive bacteria which poison the body by their metabolites. Mechnikov's observation of antagonistic microorganisms paved the way to the science of antibiotics.

Treatment of sewage with microorganisms is similar in its character to the processes by which organic and mineral substances are transformed in soil. In this connection it is expedient to dwell on the works by the Russian scientists who studied soil.

P. A. Kostychev (1845-1895) proved that microorganisms play an important role in the formation of soil humus. He studied the processes by which proteinous substances are accumulated in soils and which are also connected with the life of microorganisms.

S. N. Vinogradsky was an important figure in microbiology. He studied sulphur bacteria (1887), iron bacteria (1888), nitrifying bacteria (1890) and his works are of great scientific and practical importance. These bacteria can develop on media free from organic substances and synthesize component parts of their own bodies from carbon or carbon dioxide. The necessary energy these bacteria obtain from biochemical processes occurring during oxidation of ammonia to nitrites and nitrates, or of ferrous iron to ferric iron. This special synthesis of organic substance from carbon dioxide and water is called *chemosynthesis*. This discovery has become a remarkable event in physiology of microorganisms.

Later Vinogradsky discovered a freely existing anaerobic nitrogen-fixing bacteria, *Clostridium pasteurianum*. Numerous experiments with the culture of the isolated microorganism cultivated on media containing various forms of fixed nitrogen and various sources of carbon have shown that the decomposition of 1 g of sugar fixes 2.5-3.0 mg of atmospheric nitrogen provided the medium does not contain bound nitrogen compounds. If nitrogen is a part of the medium, the nitrogen-fixing activity of this bacterium first decreases and then disappears.

Later Beijerinck isolated an aerobic nitrogen-fixing microorganism, *Azotobacter* from soil microflora. The discovery of these microbes in soil explains the steady increase in the nitrogen content of soil which could not be explained till this discovery.

A valuable contribution to the study of the decomposition of organic nitrogen-containing compounds has been made by V. S. Butkevich. He established that the accumulation of ammonia during ammoniation is strictly coordinated with the presence of carbohydrates. If there are no carbohydrates in the medium, microorganisms use much proteinous substances for their respiration, while the nitrogen of oxidized amino acids is accumulated as ammonia. In the presence of carbohydrates, the proteinous substances are not so much used and the accumulation of ammonia markedly decreases and sometimes completely stops. These regularities are very important for the fermentation of sewage sludge.

Along with the processes by which nitrogen compounds are converted, it is interesting to consider the transformations of nitrogen-free substances, e.g. cellulose. Mineralization of cellulose was studied by V. L. Omelyansky. He showed that soil contains profuse microflora which destroys cellulose in anaerobic conditions.

The anaerobic and especially aerobic decomposition of cellulose was later studied by A. A. Imshenetsky, V. V. Pervozvanny and other Soviet microbiologists.

The decomposition of other stable organic compounds was also the object of intense investigation of scientists. Hydrocarbon, fats and similar compounds are very important in the circulation of carbon in nature. The Russian investigator V. O. Tauson dedicated many of his works to the decomposition of carbon-containing compounds. He isolated bacteria which decompose petroleum hydrocarbons, e.g. petrol, kerosine, various paraffins, benzene, xylene, cumene, phenanthrene and others. All these compounds are a good source of carbon for many bacteria.

Further study of bacteria consuming carbohydrates (V. S. Butkevich, G. A. Mogilevsky) has shown that some of them can be used as biological indicators in the prospecting of gas and petroleum.

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## 11.2. Morphology of Bacteria

*Morphology* is the branch of biology dealing with the form and structure of organisms.

**Size of bacteria.** The most important object of microbiological studies is bacteria. These are the minutest organisms which can be attributed to both the animal kingdom (for example by their ability to move) and to the plant world (by their solid shell).

Most unicellular organisms are referred to the group of bacteria which are seen with a microscope. They are characterized by simplicity of their form. The size of these microbes, measured in microns, varies within a wide range. For example, the diameter of sphere-shaped bacteria (cocci) is 1-2  $\mu$  while some multicellular sulphur bacteria size from 18 (*Thiophysia volutans*) to 50  $\mu$  (*Beggiatoa mirabilis*).

Cylindrical, or rod-shaped bacteria (bacilli) are also very small, and the ratio of the width to the length of their bodies varies greatly as well. One drop of water can contain a few billions of bacilli. The mass of  $2 \times 10^{12}$  bacteria of medium size is only one gramme.

**Shapes of Bacteria.** The shapes of bacteria are quite few. All known bacteria (and their number is over 3000) can be divided by their shape into three main groups, viz., spherical *cocci*, rod-shaped *bacilli*, and spiral-shaped *spirillae*.

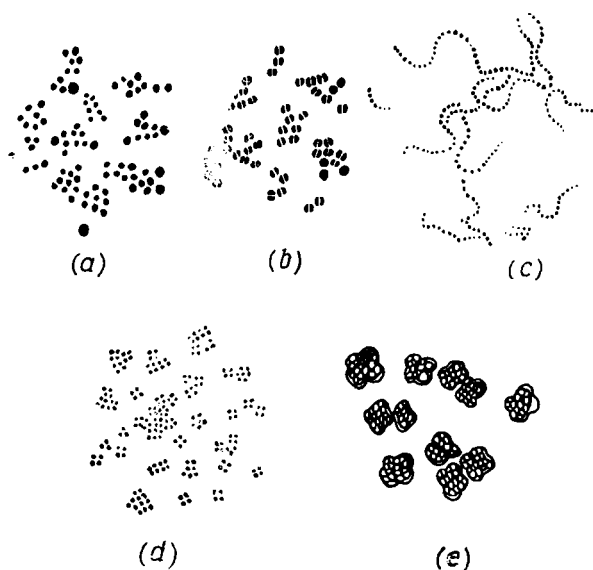


Fig. 11.1. Sphere-shaped bacteria (cocci):

a—single cocci (1000  $\times$ ); b—cocci combined in pairs (1000  $\times$ ), c—cocci joined in chains (900  $\times$ ); d—spheres joined in fours (900  $\times$ ); e—spheres joined in eights (1000  $\times$ )

The simplest shape is sphere. Cocci (Fig. 11.1a) can combine in pairs to form diplococci (Fig. 11.1b), chains (streptococci, Fig. 11.1c), or join in fours (tetrads, Fig. 11.1d), eights and unions containing more than eight cells (Fig. 11.1e).

Rod-shaped bacteria have greater variety of forms. They can join in pairs or in chains.

The appearance is not a reliable characteristic, since microbes of similar shapes can differ in their ability to form spores and their physiological properties.

All rod-shaped forms which do not form spores are called *bacteria* (Fig. 11.2a) while sporeforming microbes are called *bacilli* (Fig. 11.2b). Spiral-shaped microbes are, for example, *vibrios* (Fig. 11.3a) which can be slightly curved, vibrios, strongly curved (with several coils) *spirillae* (Fig. 11.3b), and very strongly curved (with larger coils) *spirochetes* (Fig. 11.3c).

Along with unicellular forms, there are also multicellular organisms, filamentous bacteria (Fig. 11.4).

A drop of sewage can contain all forms of bacteria. These can be accumulations of bacteria (zooglea), long chains of cocci and rods of various length, and single large spirillae. Rods, however, prevail among other forms.

The great majority of bacteria are devoid of any colour and are transparent. To make them visible they are stained.

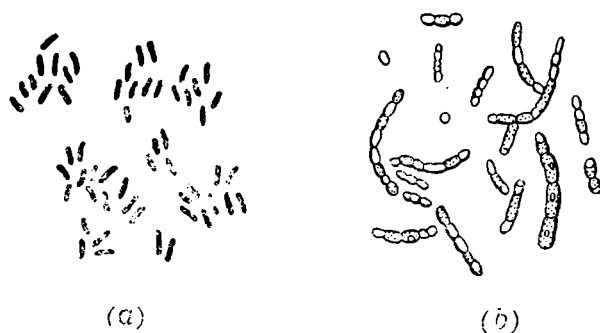


Fig. 11.2. Rod-shaped bacteria:  
a—shape; b—sporeforming bacteria (1000  $\times$ )

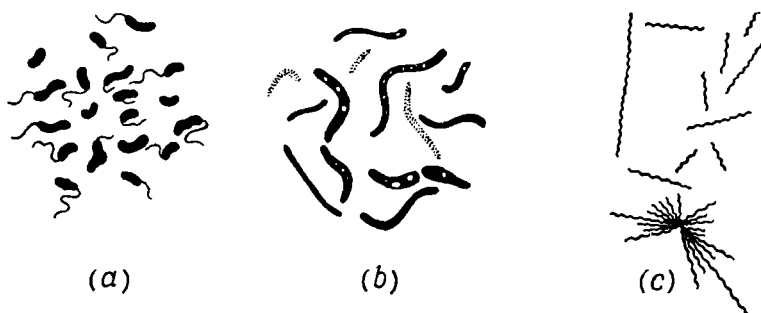


Fig. 11.3. Spirillaceae bacteria:  
a—slightly curved vibrios (1000  $\times$ ); b—spirilla, strongly curved forms (800  $\times$ ); c—very strongly curved spirochete (1000  $\times$ )

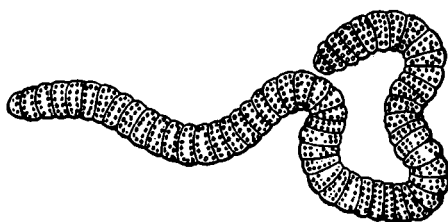


Fig. 11.4. Filamentous bacteria (150  $\times$ )

### 11.3. Filamentous Bacteria

*Filamentous bacteria* are of great importance in practical sanitary investigations. These are macromicrobes, the largest bacteria which can be seen with an unaided eye. They differ from common bacteria only in their size. For example, the largest filamentous bacteria

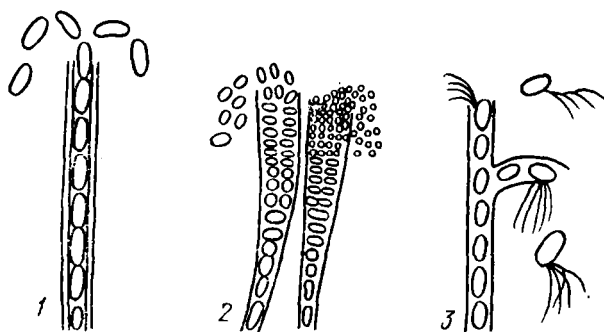


Fig. 11.5. Formation of gonidia in filamentous bacteria:  
1—Chlomydothrix; 2—Crenothrix; 3—Cladothrix

have the same action as the minutest representatives of the same group. Sulphur bacteria and iron bacteria belong to the filamentous bacteria.

Filamentous bacteria can float freely or be attached. Some filaments can be coated with mucosa, which is a kind of a case filled with  $\text{Fe}(\text{OH})_3$ .

Filamentous bacteria are reproduced by gonidia and conidia, special spore-like oblong bodies arising from the terminal cells of the filaments. Gonidia ripen in the mother filament and detached from the main membrane through a hole formed by that time in the end cell. If the cells are provided with organs of locomotion they are called gonidia, and immobile cells are called conidia. Both can produce a new filament similar to the mother filament. But the gonidia of some bacteria can attach themselves to underwater objects and divide to form a new filament and repeat the life cycle. Sometimes gonidia can grow inside the mother filament, which begins branching (Fig. 11.5).

Both spore-like formations are resistant to the absence of moisture, to the sun light, and some weak disinfectants, but are destroyed by heating, like the vegetative cells from which they originate.

Filamentous bacteria are a nuisance in water supply. Colonies of iron bacteria and their metabolites clog the pipes to obstruct the water flow.

Sulphur bacteria produce sulphuric acid. Water becomes aggressive (sulphate aggressiveness) to destroy reinforced concrete and wood structures.

## 11.4. Changeability of Microorganisms

An attempt to classify bacteria was made in 1870. There existed two opinions at that time. One of them, known as *monomorphism*, consisted in that bacteria were considered as being strictly differen-

tiated by species which were characterized by great constancy.

The other concept, known as *polymorphism*, admitted that species could vary within certain limits, and that there was no sharp division line between separate species. The adepts of this theory supposed that bacteria could sharply change their morphological and physiological characteristics depending on the conditions of their growth. This disputable problem was solved by isolation of 'pure culture' by the German scientist Koch. He showed that bacterial species sharply differ from one another. But Koch also showed that bacteria can easily change their properties depending on the medium in which they grow and under the effect of various physical, chemical and biological factors. The conditions of life have their effect on the properties of microorganisms and cause adaptation, which in turn can give rise to a new variety of bacteria, called *strain*.

For example, a prolonged action of certain climatic conditions on bacteria form geographical races of bacteria characterized by certain sets of signs which persist from one generation to another.

The bacteria of the northern seas grow better at temperatures 10°C in a medium containing salts, in conditions characterized by certain osmotic pressure. Most bacteria live in media having the salt concentration to 1 per cent. Sea bacteria require the salt concentration to 10 per cent. Bacteria living in the Transcaucasian lake Gus-chun-dag are adapted to the salt concentration of 36 per cent. Microbes living in waters with high salt concentrations are called *halophiles*.

Of all microorganisms, viruses change most easily. Their changeability is explained by their parasitic mode of life. They are not protected against the external actions and are therefore easily changed by them.

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## 11.5. Structure of Bacterial Cell

**External Membrane.** The outer membrane of a bacterium is porous, thin, colourless, and can be seen with the microscope only in large bacteria. The outer membrane gives shapes to bacteria.

The cell wall is about 10 to 50 per cent of the dry mass of the microorganisms. The proportion of the dry substance in the cell wall changes during its growth and usually increases with age. The cell wall withstands significant osmotic pressure due to soluble substances contained inside the brittle cytoplasmic membrane.

The cell wall of the microorganisms is their important organoid taking part in the metabolism. It ensures the uptake of nutrients by the cell and the excretion of the metabolites and many hydrolytic enzymes.

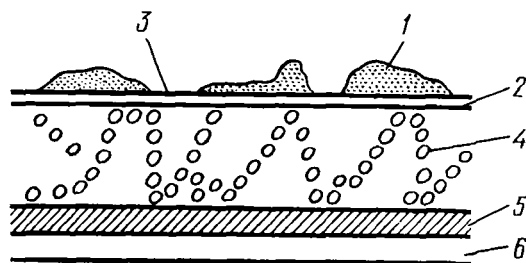


Fig. 11.6. Section of *Escherichia coli* wall:

1—lipoid layer with tubercles; 2—lipopolysaccharide layer; 3—channels; 4—loosely packed molecules of protein; 5—dense glycopeptide layer; 6—cytoplasmic membrane

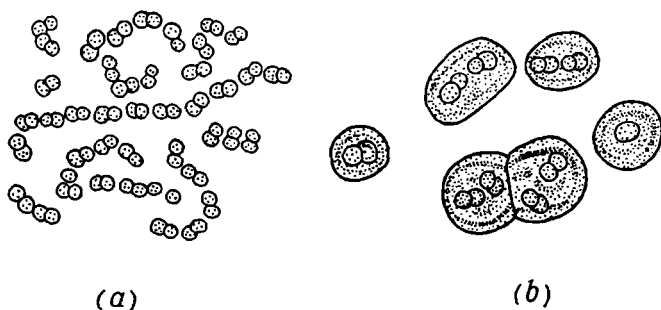


Fig. 11.7. Colonies of bacteria (1000  $\times$ ):

a—cells without capsules; b—cells in capsules

It is supposed that the initial oxidation stages occur at the interface between the cell wall and the cytoplasm, because the corresponding enzymes are found in this region. The cell wall in a certain degree controls the entrance of nutrients into the cytoplasm although they do not undergo significant changes in this process.

The chemical composition of the membrane is not uniform and differs greatly from the membranes of higher plants. The plant membrane consists of cellulose, while the bacterial membranes comprise nitrogen-free and nitrogen-containing compounds. Nitrogen-free compounds are mainly hemicelluloses, specific polysaccharides and lipoids (fat-like organic compounds). The nitrogen-containing compound is chitin (a polysaccharide type organic substance consisting of acetylated glucosamine).

The cell wall has a laminar structure (Fig. 11.6). Its surface layer consists of lipid tubercles and processes.

It rests on a lipopolysaccharide layer, and the underlying layer consists of loosely packed protein molecules and a dense glycopeptide layer attached to the cytoplasmic membrane. The entire mass is passed through with channels and the cell wall is therefore

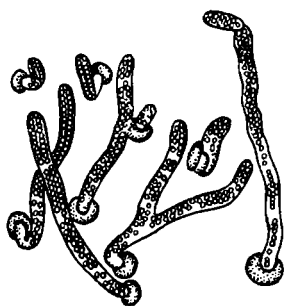


Fig. 11.8. *Thiothrix nivea*  
(1000 ×)

penetrable to salts and many other molecular compounds. Unlike the cell wall, the cytoplasmic membrane is semipermeable and it controls the uptake of nutrients by the cell. The cytoplasmic membrane is a continuous structure of about 7.5 m $\mu$  thick. Its inner layer is supposed to be of lipid, while the outer layer, of proteins. The distance between the layers is the doubled length of fatty acid chains. The membrane also contains small quantities of carbohydrates, RNA and DNA.

The cytoplasmic membrane of a microorganism performs the following four functions: (1) it acts as an osmotic barrier; (2) it acts like an organelle concentrating nutrients inside the cell and promoting excretion of metabolites; (3) it is the site of biosynthesis of some component parts of the cell, especially of the components of its wall and the capsule; (4) it is the site of localization of some enzymes and organelles, such as, e.g. ribosome\*.

As a cell ages, the membrane can swell and become coated with mucilage, especially in cultures grown on media rich in carbohydrates and depleted of proteins. The outer layers of the membrane are converted into a gelatinous sticky mass to form a *capsule*. The size of the capsule is often greater than the bacterium itself and of intricate shapes. Mucilage often coats several cells simultaneously inside one capsule. Such colonies of bacteria embedded in a gelatinous matrix are called *zooglea* (Fig. 11.7b).

The gelatinous matrix of filamentous bacteria is a morphological adaptation to the environment and is not connected with unfavourable conditions of the nutrient medium. For example, a gelatinous pad is formed at one end of a sulphur bacterium of the genus *Thiothrix*, by which it attaches itself to immovable objects (Fig. 11.8).

Macromolecules containing ionogenic groups, which are responsible for the charge on the cell, are located on the surface of the cell wall. The surface of the microbial cell bears a negative charge because the surface components contain compounds whose isoelectrical state is in the acid medium. Some organisms are not polarized, because the charge is distributed uniformly over the entire surface.

Electrophoretic mobility of microorganisms depends on their species, the ionic strength of the solution and the pH of the medium.

**Bacterial Cytoplasm.** The cell content enclosed by its walls is called *protoplast*. It consists of the cytoplasmic membrane and the

\* Ribosomes (polyribosomes) are the site of protein synthesis. Ribosomes consist of 40-60 per cent of RNA and 60-40 per cent of protein.

'live' matter of the cell, the cytoplasm, or protoplasm. The cytoplasm of bacteria is a colourless, translucent, slightly viscid substance.

By its physico-chemical structure, the cytoplasm is a colloidal formation, in which particles of various chemical nature are dispersed in water. The cytoplasm comprises proteins, sulphur, fats, and other inclusions (Fig. 11.9).

Among the inclusions, of certain interest are volutin granules, which are actually nucleoproteins. These granules are found at the ends of the bacterial cells. Many smaller granules are

directly connected with the enzymes and their activity.

About one fifth volume of the cell interior is filled with DNA. From 20,000 to 30,000 ribosomes surround it. They consist of about 40 per cent of protein and 60 per cent of RNA. The remaining space in the cell is filled with water (dispersion medium) with the enzymes dissolved in it, and also with organic and inorganic monomer molecules.

The cytoplasm contains also other biologically important granules and organelles, such as mitochondria\*, ribosomes and lysosomes\*\*. The most important enzymatic reactions occur in the cytoplasm and its organelles, and in microscopic and submicroscopic inclusions. The cytoplasm continually changes to absorb new substances and to impose various chemical changes on them. Potential energy of large molecules (proteins, fats and carbohydrates) is converted into kinetic energy during their splitting into simpler compounds. The cytoplasm of bacterial cells is characterized by highly intense metabolism.

Cytoplasm has the properties of living matter and is characterized by relative species stability. It can continuously renew its inner

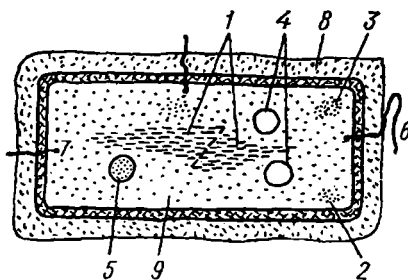


Fig. 11.9. Rod-shaped bacterium:

1—nucleus substance with indistinct shape and distribution; 2—cytoplasm; 3—dense intracellular granules containing RNA; 4—structures resembling vacuoles; 5—granules of volutin, fat, polysaccharides or other nutrients; 6—flagellum; 7—granule, the point of flagellum attachment; 8—capsule; 9—protoplasmic membrane. (For the sake of clarity, the flagella and capsule are shown in the picture. As a rule, they are not found in one cell simultaneously.)

\* Mitochondria are spherical or oblong intracellular organelles rich in various enzymes. Their function is to realize oxidation reactions which are the source of energy, to transfer electrons in the chain of the components synthesizing ATP, to catalyze synthetic reactions induced by ATP, and to synthesize mitochondrial proteins.

\*\* Lysosomes are closed bags containing enzymes whose catalytic action is controlled by membranes of these organelles. Injury of the cell membrane is followed by the release of the enzymes into the cytoplasm to destroy the cell.

structure by converting nutrient substances into the complicated structure of living matter.

Sometimes fat occurs in bacteria in considerable quantity. It can be from 35 to 50 per cent of the dry microbial mass if the nutrient medium is rich in carbon and poor in nitrogen.

**Nucleus of the Bacterial Cell.** DNA makes about 1-2 per cent of the dry mass of microorganisms. DNA is a carrier of genetic information of the organism. Most microorganisms have parts where the main bulk of DNA is concentrated. This has a definite structure (organelle) and is called the *nucleus*. The nucleus is connected with the cytoplasmic membrane irrespective of the fact whether it is surrounded with elementary membranes (like in ameba) or has no such membranes (like in bacteria and blue-green algae). The nucleus substance is activated during the reproduction period and during certain age periods connected with ageing.

According to A. A. Imshenetsky, various bacteria have different types of nucleus. Some bacteria have a diffuse nucleus. Its substance is in the dispersed state, while the protoplasm of other nuclei contains separate granules of chromatin which take part in the formation of reticular or axial threads; and in some other bacteria, the chromatin granules are accumulated to form an isolated nucleus. Probably more primitive forms have diffuse nuclei while more complicated forms have nuclei of more definite structure. The nucleus of a bacterial cell can seldom be seen with the microscope.

**Plasmolysis and Turgor.** The complexity of the structure of a bacterial cell is exhibited by phenomena known as plasmolysis and turgor.

The concentration of salts in a living microbial cell is always higher than in the surrounding medium. Microbes can therefore live in weak *aqueous* solutions. By osmotic action, water enters the cell together with the substances dissolved in it. The internal osmotic pressure creates tension in the cell, known as *turgor*. If a microbe gets in a concentrated solution, whose osmotic pressure is higher than inside the cell, water is released from the cell, the protoplasm shrinks and becomes detached from the upper membrane. This is known as *plasmolysis*. The turgor of the cell can be restored if transferred into a weaker salt solution.

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## 11.6. Sporeforming in Bacteria

A *spore* is a resting stage of sporeforming types of bacteria. Some rod-shaped bacteria, when they are in unfavourable conditions, form, inside their cells, oblong or elliptic bodies which were given the name of spores (Fig. 11.10). Almost all protoplasm is consumed

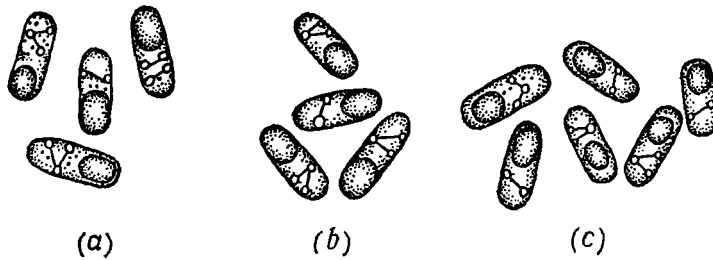


Fig. 11.10. Formation of a spore:  
a—sporogenic zone; b—prospore; c—mature spore

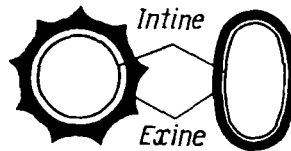


Fig. 11.11. Section of a spore

in the formation of the spores. A *prospore* is first formed, which then turns into a spore. The process by which a spore is formed takes from 40 to 50 minutes to a few hours, and sometimes it can take about 24 hours. Sporophoric cells immediately become unable to reproduce. When the spore ripens, the residues of the vegetative cell are destroyed. The external membrane, *exina* (Fig. 11.11) becomes difficultly permeable to water and the substances dissolved in it. The internal membrane, *intina*, is important for the germination of the spore. It is used for the construction of a new vegetative cell. Water is contained in the spore in a special state, the enzymes are low active, and the membrane limits the exchange of the spore with the environment. This keeps the spore alive for scores and hundreds of years. Hence, the spore is a form of bacteria stable to unfavourable effects of the environment. For example, when river water is boiled, all bacteria are killed except sporeforming ones. Spores are not killed by freezing, drying, direct sun radiation, and even strong chemical poisons. They can be killed by sterilization in autoclaves at a temperature of 120-140°C. However, one and the same bacterium can give spores of different stability, and some spores can be killed by prolonged boiling.

When a spore is set in favourable conditions, it begins growing. It swells, becomes richer in water, almost doubles in size. The external shell breaks and the germ appears through the opening. The enzymes are activated and the formation of a vegetative cell is completed in some bacilli in 40-50 minutes. When poisons are

accumulated in the medium, bacilli can lose their ability to form spores.

Although the inner structure of spores has not yet been sufficiently studied, it is known for certain that the spores contain very complicated enzyme systems ensuring the growth and respiration, and also the complete set of the genetic material. These elements are kept inside the spore and are necessary for its germination. Dipicolinic acid has been discovered in spores which is not contained in vegetative forms.

## 11.7. Locomotion of Bacteria

Only some bacteria can move about. This ability is due to the presence of flagella in them. Only motile spirochetes can move by rhythmic vibrations of the entire body. Flagella are cytoplasmic processes which remain outside the cell during plasmolysis. Unless properly stained they are not seen with the microscope. Their thickness is the same along their entire length and usually does not exceed  $1/20$ th the diameter of the bacterial cell (about  $0.02-0.05 \mu$ ). The velocity of their movement is  $10-20 \mu/\text{sec}$ .

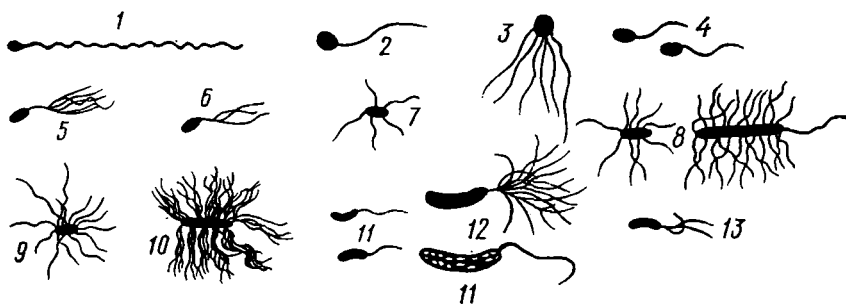


Fig. 11.12. Types of flagellates:

1, 2, 4, 11—Monotricha; 5, 6, 12, 13—Lophotricha; 3, 7, 8, 9, 10—Peritricha



Fig. 11.13. Nitrifying bacteria ( $700\times$ ):

1—*Nitrosomonas europaea* (nitrite bacteria), the monad stage; 2—the same in the zooglycal stage; 3—*Nitrosomonas javanensis* (nitrite bacteria); 4—*Bact. nitrobacter* (nitrate bacteria)

Motile bacteria are divided into three groups according to the arrangement of their flagella: (1) monotricha, a group of bacteria having one polar flagellum; (2) lophotricha, bacteria having a tuft of flagella at one end of the cell; (3) peritricha, a group of bacteria having flagella over their entire surface (Fig. 11.12).

Sometimes bacteria alternate the motile and non-motile stages. For example, nitrobacteria (oxidizing ammonium to nitrites) grow into immobile rods when placed in a fresh nutrient medium. But as the medium becomes depleted of the nutrients, the bacteria develop motility. They acquire a flagellum. In this form nitrobacteria energetically oxidize the remaining ammonium salts. This completed, the bacteria lose their flagella and precipitate to the bottom to form dense zooglea. A genus of bacteria known as *Nitrobacter* (the causative agent of the second phase of nitrification) has only one, immobile stage (Fig. 11.13).

## 11.8. Reproduction of Bacteria

Bacteria are reproduced by cell division (Fig. 11.14). First, processes develop inside the bacterial body, which later form a ring to divide the cell into two halves. But there are some bacteria (myxobacteria) which multiply by transverse division without the formation of a cell partition (Fig. 11.15). Each half quickly grows to the size of the mother cell and in turn divides into halves, etc. The conditions being favourable, the multiplication is a rapid process. Each bacterium is presumably divided in 20-30 minutes. According to Kohn, if bacteria could develop unobstructed, one bacterium of medium size ( $2\ \mu$  long and  $1\ \mu$  wide) could fill the volume occupied now by all seas and oceans within five days of free growth. But the growth of bacteria depends on many factors and they cannot grow into such fantastic volume.

The minutest size and the rapidity of reproduction of bacteria are very important for understanding of the conditions in which the microbes interact with the environment.

0.001 ml of water can hold to  $10^9$  bacteria. If this amount is added to a cubic meter of water and distributed uniformly throughout its

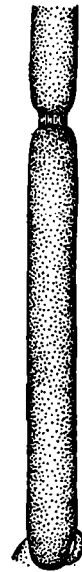


Fig. 11.14. Division of a bacterium (19,000 $\times$ )

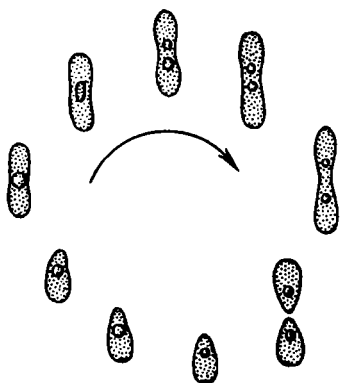


Fig. 11.15. Stages of direct cell division ( $2000\times$ )

volume, one litre of water will contain  $10^6$  bacteria or 1000 bacteria in 1 ml. Hence, even a negligibly small quantity of substance infected with pathogenic bacteria is sufficient to transmit the disease through the agency of water. The total surface of the microbial bodies is important here since the interaction between bacteria and the environment depends on the surface of contact. The overall area of microbes is immense (we mean the ratio of the microbial surface to its mass). The total surface of man is 0.04 sq.m per kg body weight, while in bacteria it is 100,000 times greater,

i.e. 4000 sq.m per kg weight. This accounts for the remarkable activity of bacteria and their extraordinary sensitivity toward changes in the environment.

## 11.9. Nutrition of Bacteria

Bacteria have no special alimentary organs. All nourishment is supplied to the cell through osmotic intake via the minutest pores in the cell membrane. These are very small and the nutrients should be very finely divided to pass them (practically to the molecular state).

When a microbe takes up nutrients, it releases biological catalysts, enzymes, into the medium. Their purpose is to dissolve the nutrients so that they can pass inside the cell through its membranes.

The nourishment is utilised in the synthesis of proteins, fats, and carbohydrates. Part of the nourishment is used for the growth of the cell, and another part is consumed for respiration.

Substances that cannot be assimilated by the cell are dissolved and excreted through the pores into the environment.

**Types of Nutrition.** Nutrition of microbes is quite varied, but their attitude to the main organogens (carbon and nitrogen) is especially characteristic.

This is very important in the treatment of water and sewage because it determines the role of microorganisms in mineralization of organic matter.

All microbes are divided into three groups by the method of taking up nutrients:

1. *Autotrophic* (Gr. *autos*, self + Gr. *trophe*, nutrition). These bacteria use carbon of mineral compounds: carbon dioxide and carbonates.

The energy required for their life these bacteria obtain by photosynthesis (assimilation of carbon dioxide by green plants and purple sulphur bacteria), or by chemosynthesis, i.e. by oxidation of ammonium, sulphur, nitrites ferrous salts, etc. These are nitrifying bacteria, iron bacteria, colourless sulphur bacteria and thionic acid bacteria.

Iron bacteria are autotrophic and can grow on media free from organic matter. To synthesize one gramme of the cell substance, these bacteria oxidize 279 g of divalent iron with formation of 534 g of  $\text{Fe}(\text{OH})_3$ . The ratio of the oxidized iron to the assimilated carbon (from carbon dioxide) is 500 : 1 and it shows what a great amount of  $\text{Fe}(\text{OH})_3$  is formed during the autotrophic growth. When a bacterium dies, ferric hydroxide serves as the material for the formation of bog ore. Water containing divalent iron can give scale in tubes and heat-exchangers if the velocity of water in them is low and the temperature drop is insignificant.

The formation of oxygen is very important during assimilation of carbon dioxide by photosynthesizing autotrophic microbes. This oxygen is used by the organisms to mineralize organic matter in aerobic conditions. The oxygen is liberated in minute bubbles on the surfaces of the aquatic plants. The bubbles can be clearly seen on a sunny day. A considerable part of the oxygen liberated into the water is immediately dissolved in it. The solubility of this oxygen in water is five times greater than the solubility of the atmospheric oxygen.

2. *Heterotrophic* (Gr. *heteros*, other) bacteria require organic substances to synthesize their body. Heterotrophic bacteria are quite numerous. These are putrefactive and fermentation bacteria, moulds, yeasts, actinomycetes. This group of microbes is called *saprophytes* (living on decaying organic matter).

3. *Paratrophic* bacteria require living material (protein). These are pathogenic microbes. They are called parasitic bacteria since they are dependent on a living host for their nutrition.

There are however many transient forms of bacteria.

**Metabolism.** This is the sum of all the biochemical processes by which the living cell is maintained. The energy required for metabolism is obtained by the living cell from biochemical conversion of chemical substances having high potential energy.

Hence, the constructive energy exchange is the fundamental principle upon which the life of an organism rests. As microorganisms live, they can, within a certain limit, change the conditions of the medium which they inhabit. They spend materials and energy to change the active reaction of the medium (liberation of acid or alkali), to render harmless toxic substances, etc. These biochemical processes are called the *adaptation metabolism*.

The composition of substances in the animal, plant and microorganism tissues differs only insignificantly. Proteins of all living cells consist of twenty main amino acids. The most important components of the living tissue, nucleic acids, have similar structures and their components are common for all living organisms. The differences between the types of cells reside only in details of structure, in the arrangement of specific macromolecules or protoplasmic structures and specific characteristics of metabolism.

The methods by which energy is produced in the animal, plant and microorganism tissues are similar in principle. The feature of biological oxidation is that part of free energy is accumulated in macroergic bonds of adenosine triphosphoric acid. Another part of the energy is dissipated as heat. Microorganism, plant, and animal cells utilize the energy of macroergic bonds of the acid to meet the own energy needs.

The biological oxidation is accompanied by phosphorylation. Adenosine diphosphoric acid which is one of the most important enzyme of the cell, is combined with the group  $\text{PO}_4^{3-}$  to form adenosine triphosphoric acid. When ATP is formed, the potential energy of this compound increases to 80 kilocalories/mole, which is then released during the breakdown of the macroergic phosphate bonds.

**Enzymes.** These take an active part in all biological processes connected with the life of a living cell.

Enzymes are catalysts synthesized by a living cell. Like any other catalyst, they decrease the energy of activation of a system by forming unstable intermediate compounds with the substrate.

All enzymes are protein complexes. They have the properties of hydrophilic colloids with high surface energy and are therefore sensitive to various environmental factors. The enzyme activity decreases with sharp changes in temperature and pH of the medium, with increasing osmotic pressure, excess concentration of the substrate, accumulation of metabolites, by the action of bactericidal rays, increased concentration of the enzymes themselves, etc. The activity of the enzymes is the highest at a temperature of 25-35°C. Most enzymes are destroyed at a temperature of 55-60°C.

The change in the pH of the medium can cause coagulation of the enzymes. But the enzymes are closely connected with the cytoplasm of the cell which has a high buffer capacity ensuring constant pH inside the cell.

Extraneous substances have their effects of the enzyme activity. Substances activating enzymes are called *activators* and those slowing down their activity are called *inhibitors*.

The action of some enzymes is blocked with poisons, e.g. sulphad drugs, antibiotics, narcotics, cyanides, dyes,  $\text{H}_2\text{S}$ , CO, and disinfectants.

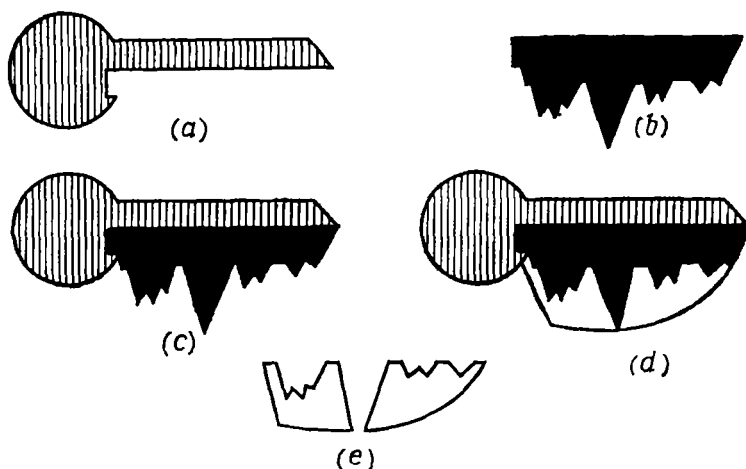


Fig. 11.16. Action of an ecto enzyme:

*a*—apoenzyme (protein of enzyme); *b*—coenzyme (nonprotein part of an enzyme having a specific activity); *c*—enzyme; *d*—transient union of the enzyme with the substrate; *e*—split substrate

The mechanism of poisoning of catalysts consists in that the active centres of the enzyme and poisons form stable compounds, which make the enzyme inaccessible to the substrate.

Any factor acting on the enzymes acts on the microorganisms since the physiological processes occurring in a microbial cell almost completely depend on the enzyme activity.

The molecules of most enzymes consist of two main components which are inactive when taken separately: (a) thermolabile protein, called the carrier, or *apoenzyme*, and (b) a nonprotein component, thermostable component called *coenzyme*, playing a very important role in the enzyme action. The two components make a complete enzyme, *holoenzyme*.

By the site of their action the enzymes are classified into *ecto-enzymes* and *endo-enzymes*. The former act outside and the latter inside the cell. Ecto-enzymes mainly catalyze hydrolytic reactions, while endo-enzymes catalyze the reactions occurring inside the cell, connected with the synthesis or the release of energy (respiration, or biological oxidation). Hence ecto-enzymes prepare the nutrients before they are taken inside the cell, while endo-enzymes promote the assimilation of nourishment inside the microbial cell.

The mechanism of action of ecto-enzymes is shown schematically in Fig. 11.16.

The action of enzymes is strictly specific. Their specificity is due to the structural correspondence of the molecule of the substrate to the enzyme molecule. Like a key opens only one lock, the enzyme can act only on a certain substrate.

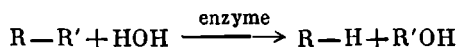
All living cells have a natural set of the appropriate enzyme systems which is characteristic of all cells of a given type. These are called *constitutive* enzymes.

There exists another group of enzymes which appear inside a cell by the action of the surrounding medium. These newly synthesized enzymes are the response of the cell to the new environmental conditions. They are called *induced* or *adaptive* enzymes.

*Classification of Enzymes\**. All enzymes are divided into six classes according to their action.

1. *Oxidoreductases*, the enzymes catalyzing oxidation-reduction reactions. The enzymes belonging to this class accelerate direct or indirect oxidation of substances. These are e.g. *dehydrogenases* which catalyse the oxidation-reduction processes by hydrogen proton transfer from one molecule to another.

2. *Hydrolases*, the enzymes that catalyze the hydrolytic cleavage of organic substances by breaking down the intramolecular bonds according to this scheme:



These enzymes are, e.g. amylases *Bac. subtilis*, which are divided into two groups, of which one hydrolyses carbohydrates (starch, dextrin, glycogen, amylose, amylopectins) to 30-40 per cent, and is called diluting, while the other group hydrolyzes the substrate to 50-60 per cent (saccharifying enzymes).

3. *Transferases*, the enzymes that catalyze the transfer of various chemical groups from one molecule to another. For example, transaminase accelerates the transfer of the group  $-NH_2$ ; transmethylase catalyzes the transfer of the group  $-CH_3$ ; and transketolase, of  $-C=O$  (keto-group).

4. *Lyases*, the enzymes accelerating the formation of double bonds or attachment of atoms at the point of double bonds.

5. *Isomerases*, the enzymes catalyzing the isomeric transformations of substances.

6. *Ligases*, the enzymes accelerating the synthesis of proteins, nucleic acids, fatty acids, and other organic compounds inside the living cell.

## 11.10. Chemical Composition of Bacteria

Water makes about 80-85 per cent of microorganism mass. The major part of water is in the bound state (in colloidal particles).

\* All enzymes have the ending "ase".

It has been established that cells of almost all microorganisms are alike with respect to their chemical composition and comprise the same types of macromolecules: proteins, nucleic acids, polysaccharides, lipids. Organogens have been found in the biomass of microorganisms, such as carbon, nitrogen, oxygen and hydrogen, whose content is 90-97 per cent of the dry weight. The proportion of the other very important elements which are vitally important for microorganisms (P, S, K, Ca, Mg, Fe, Na, Cl, Mn, etc.) is 3-10 per cent of the cell substance.

The average composition of a microorganism cell is (in per cent): carbon 51.1, oxygen 33.7, nitrogen 8.7 and hydrogen 6.5; the empirical formula of the biomass is  $C_{14}H_{21}O_7N_2$ , and of the bacterial mass,  $C_5H_8O_2N$ . The most important component part of a living cell is protein. Its content varies from 8 to 14 per cent. Carbohydrates are meagre; they are contained mainly as monosaccharides and glycogen. The average fat content is 1-4 per cent, but some microorganisms accumulate fat to 30 per cent.

In addition to these components, the microbial cell contains minute quantities of the other ash elements: P, K, Ca, Mg, S, Na, Fe, Mn, Br, Cl, Co, Ni, Ag, Zn, W, Cd, V, Al, etc.

The quantities of these elements vary, and depend on the microbe type and the conditions of their life. The importance of these elements for the metabolism of a microbial cell is very great. The absence of either of them inhibits metabolism.

The function of the mineral elements is to activate various enzymes. Iron, for example, is necessary to synthesize catalase, while zinc is required for the action of alcohol dehydrogenase. Magnesium activates some enzymes (such as hexokinase) and is also very important in the regulation of the ribosome particle aggregation.

The enzyme activation with ions is not always specific. For example, isocitratelias of *Pseudomonas aeruginosa* cells is activated by the ions  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Co^{2+}$ . Cases of ion antagonism are known where one ion masks the effect produced by the other ion. Some enzymes of extremely halophilic bacteria (characterized by affinity for 20-30 per cent of NaCl) are adapted to high concentrations of common salt and function in these conditions. The enzymes of moderately (5-20 per cent) and weakly (2-5 per cent NaCl) halophilic bacteria do not show high activity in the presence of sodium chloride.

Ribosomes of highly halophilic bacteria, in contrast to ribosomes of other bacteria, require high concentration of  $K^+$  to neutralize amino acid radicals of the ribosome protein.

The ion  $Na^+$  is necessary to absorb dissolved substances from the surrounding medium. For example, to absorb glutamate, *Halobacterium salinarium* badly needs  $Na^+$  ion just like sea *Pseudomonas* needs it to absorb sugars and some amino acids.

All necessary substances microorganisms obtain from the surrounding medium together with nutrients. In addition to the mentioned elements, many vitamins are necessary for normal life of microorganisms. Vitamins promote energy processes and synthesis of the cell substance. About 15 vitamins are known which are necessary to microorganisms because these substances are coenzymes or their components. The following vitamins, or their analogues, are especially important: (1) thiamine (vitamin B<sub>1</sub>); (2) biotin (vitamin B<sub>7</sub>); (3) nicotinic acid (PP factor); (4) riboflavin (vitamin B<sub>2</sub>); (5) pyridoxine, pyridoxal, pyridoxamine (vitamin B<sub>6</sub>); (6) pantothenic acid (vitamin B<sub>5</sub>, calcium salt); (7) lipoic acid (component part of vitamin B complex); (8) tetrahydrofolic acid (component part of vitamin B complex); (9) *para*-aminobenzoic acid.

The attitude of microorganisms to vitamins is very different. Some of them synthesize vitamins themselves, while the others do not have this property and require the presence of vitamins in the nutrient medium. For example, microorganisms do not grow if either of the vitamins PP, B<sub>1</sub>, B<sub>2</sub>, or B<sub>7</sub> promoting their growth is absent, and if the quantity of a given vitamin is deficient, the growth is slowed down.

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## 11.11. Respiration of Bacteria

Like higher organisms, microbes breathe to receive energy necessary for their growth, multiplication and movement. Hence all vital processes occurring in them consume energy which is received from chemical conversions of substances having high potential energy (proteins, fats, carbohydrates).

Respiration in microbiology means biological oxidation with liberation of energy. Any biological oxidation process in a bacterial cell is a modification of chemical reactions of the following types:

- (a) direct oxidation by oxygen;
- (b) indirect oxidation without oxygen.

These processes occur in the presence of biological catalysts, endo-enzymes, which are present inside the cell.

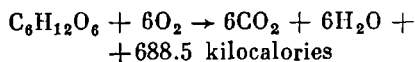
All bacteria are classified as *aerobic* and *anaerobic* by the method of their breathing. Aerobes, for example, acetic acid bacteria, moulds, nitrifying and other bacteria need free access of oxygen.

Another type of respiration does not require oxygen which is detrimental to anaerobes. This group of microorganisms are butyric acid bacteria, methane bacteria, etc.

Some microorganisms can live in both the presence and absence of atmospheric oxygen. These are called *facultative* anaerobes, such as, for example, lactic acid bacteria, yeast, etc.

Figure 11.17 shows the growth of various microbes on nutrient media.

An example of oxygen respiration is the process of glucose oxidation to water and carbon dioxide:



An intricate chain of conversions stands behind this summary equation. This chain of enzymatic processes has been well studied and appeared to be the same for animals, plants and microorganisms.

Respiration with oxidation of glucose consists of the following stages:

(1) Formation of an ester of sugar and phosphoric acid with conversion into ATP and ADP. Formed first is glucose-6-phosphate and then fructoso-1,6-diphosphate. *Phosphorylation* in this process decreases the activation energy of the system to activate the substance to be oxidized.

(2) Cleavage of the diphosphoric ester of glucose into 2-triosophosphate: 3-phosphoglyceraldehyde and dihydroxyacetone phosphate, which are readily converted into one another.

(3) Oxidation of 3-phosphoglyceraldehyde (2 molecules per 1 molecule of glucose) to 1,3-diphosphoglyceric acid. In this process, hydrogen is combined with the special enzyme, nicotinamide adenine dinucleotide (NAD) to liberate energy. Part of the energy is consumed for the attachment of the phosphate radical to adenosine diphosphate (ADP) which is converted into adenosine triphosphate (ATP).

(4) Oxidation of 3-phosphoglycerate to pyruvic acid. Two ATP molecules are also formed in the process. (During the glycolytic period of respiration, i.e. without oxygen, 4 molecules of ATP are formed for one molecule of glucose; two ATP molecules are spent for its phosphorylation.)

(5) Pyruvic acid enters the tricarmonic cycle. This complicated cyclic conversion is accompanied by the formation of several acids containing 4, 5, and 6 carbon atoms and liberation of three  $\text{CO}_2$  molecules.

(6) The hydrogen of pyruvic acid, which is gradually eliminated from carbon in anaerobic conditions, is used in the respiration chain through several oxidation enzymes.

The enzymes which handle the hydrogen are dehydrogenases. These are proteins carrying the coenzyme, di- or triphosphopyridine

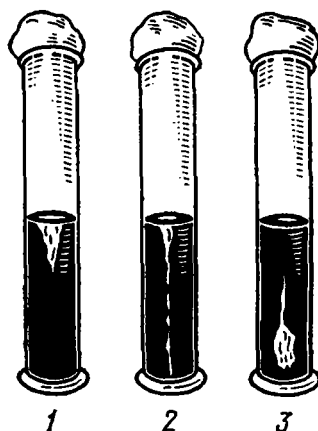
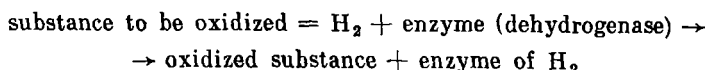


Fig. 11.17. Stab cultures of (1) aerobes; (2) facultative anaerobes; and (3) anaerobes

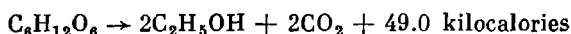
nucleotides (NAD or NADP). The process can be shown schematically as follows:



The hydrogen obtained by dehydrogenase is attached to flavine enzymes. The hydrogen is then combined with oxygen to give water.

The oxidation of one mole of sugar gives 38 moles of ATP which strongly increases the potential energy of the system and is spent for the vital processes of the cell.

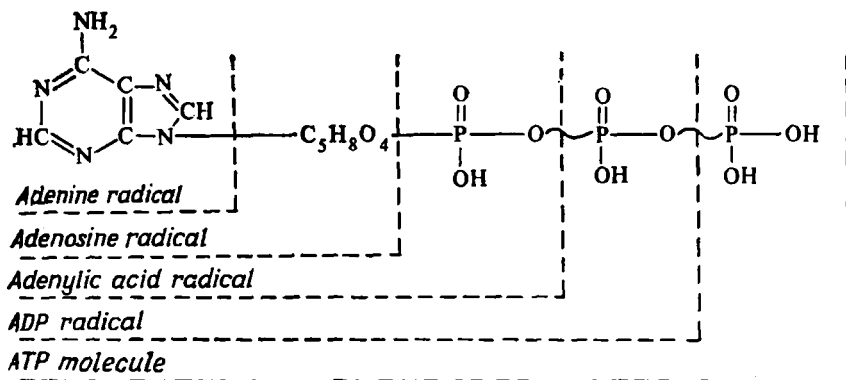
The respiration of anaerobes is effected in the absence of oxygen. The required energy is obtained by them from the cleavage of complicated molecules of organic matter into their simpler components. The amount of thus obtained energy is considerably less than with aerobic respiration\*. Glucose fermentation is an example of anaerobic respiration:



*Fermentation* is an anaerobic decomposition of carbohydrates and the related substances into products which are not further decomposed by the enzymes unless molecular oxygen is available.

Carbohydrates are decomposed by a series of processes, each of which is catalyzed by its own enzyme. These processes are divided into two types: oxidation-reduction processes, and those connected with the transfer of phosphates. The former reactions supply energy, while the latter processes transfer this energy. Adenosine is the carrier of phosphate ions.

Adenosine, being in either of the following three phosphorylated forms—adenosine monophosphate (adenylic acid), adenosine diphosphate, or adenosine triphosphate—can transfer one, two, or three phosphate groups respectively:



\* Anaerobic (glycolytic) respiration gives only two free molecules of ATP.

All these esterification processes are endothermic. The conversion of adenosine into adenylic acid requires 3 kilocalories per one mole; the conversion of the acid into ADP requires 9 kilocalories per mole, and the conversion of ADP into ATP requires 11 kilocalories per mole. The consumption of much energy is shown by a curved line at the point of bond:  $O \sim P$ . The inner energy of these compounds increases during their formation. This energy is released in the process of phosphate group transfer. This energy is consumed by the living organisms for their vital processes.

Anaerobic processes are used to digest sewage sludge. Because of the low heat effect of the reaction, the anaerobic process is convenient in the treatment of sewage because large amounts of organic matter are processed during the synthesis of microbial cells.

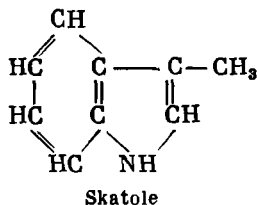
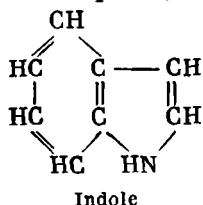
Some authors explain anaerobiosis by the absence of the enzyme catalase in anaerobes which decomposes hydrogen peroxide. They suggest that organic matter gives hydrogen peroxide at the first stage of its oxidation with atmospheric oxygen, while hydrogen peroxide is poison for all living cells. But all microbes, except anaerobes, can release the enzyme catalase into the surrounding medium which decomposes hydrogen peroxide into water and oxygen. Anaerobes are poisoned with hydrogen peroxide in the presence of oxygen.

All processes are classified as aerobic and anaerobic depending on whether aerobic or anaerobic organisms are involved.

## 11.12. Role of Microorganisms in Matter Cycle

Microorganisms use carbon of various compounds to build up their bodies and are therefore active participants in the conversion of carbon-containing compounds in nature. This can be illustrated by the carbon cycle in nature shown in Fig. 11.18.

Biochemical decomposition of proteins is of great practical importance. The decay of proteins or their derivatives under the action of putrefactive bacteria is called putrefaction, which can be aerobic and anaerobic. Putrefaction liberates substances characterized by strong and unpleasant odour: ammonia, hydrogen sulphide, skatole, indole, mercaptans, etc.:



Mercaptan

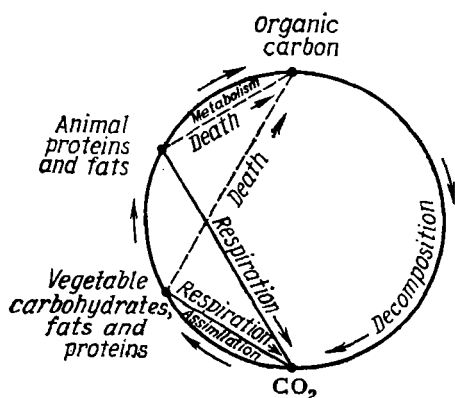
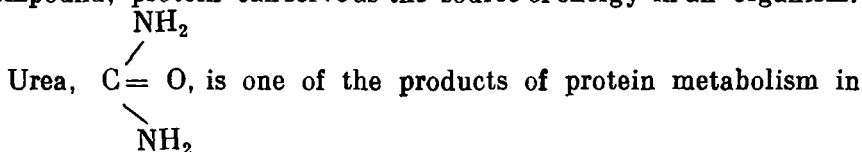


Fig. 11.18. Carbon circulation in nature

But proteins do not always decompose to these compounds. For example, during mineralization of organic matter at sewage treatment plants, proteins are destroyed to the products which have no unpleasant odour.

Microorganisms mostly utilize the nitrogen of proteins in the form of intermediate decomposition products (aminoacids) and in the form of end products, ammonium salts, for the secondary synthesis of proteins. But protein con-

tains other organogens (C, P, S, H, O) which are necessary for the construction of a bacterial cell. Moreover, being a high-molecular compound, protein can serve as the source of energy in an organism.

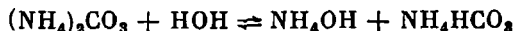


is one of the products of protein metabolism in a living body. Microorganisms (especially urobacteria) hydrolyse urea in the sewage system according to the equation:



This process can occur in both aerobic and anaerobic conditions.

Ammonium carbonate, being a salt of a weak acid and a weak base, easily hydrolyzes:



Ammonium hydroxide is characterized by the equilibrium:



which explains the smell of ammonia in lavatories.

In the process of nitrification, the nitrogen of ammonium salts is oxidized to nitrites and nitrates. This process occurs in two phases under the effect of two types of microorganisms. The first phase is activated by *Nitrosomonas*:



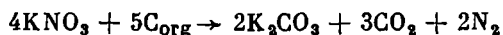
The second phase (oxidation of nitrites to nitrates) depends on *Nitrobacter*



The oxidation is very slow. Experiments have shown that 10 mg of ammonium nitrogen are oxidized to nitrites during 15 days and 10 mg of nitrites are nitrated during 40 days (in the same conditions).

Temperature has a great effect on the rate of nitrification. The variation of temperature in the range from 9 to 26°C does not produce appreciable effect on the velocity of the process, but as the temperature drops below 9°C, the process is slowed down, at 6°C the decrease in the reaction rate is very marked, and at 0°C nitrification is practically discontinued.\*

There are microorganisms which induce denitrification, i.e. reduction of nitrates to nitrogen gas. The denitrifying bacteria are facultative anaerobes. Denitrification occurs in the medium of nitrogen-free compounds, such as carbohydrates, cellulose, salts of volatile fatty acids, etc. These substances are oxidized by the oxygen liberated from nitrates. Probably this is the explanation of this process from the energy point of view. Schematically this process can be written as this



These processes proceed in the absence of free oxygen and in the presence of organic matter and nitrates. They widely occur in nature.

Denitrification processes can occur in the absence of organic matter and in the presence of sulphur:



This process is induced by the microbe *Thiobacterium denitrificans* and can occur in some structures of sewage systems which are not washed with effluents (vaults, ceilings, walls).

There are microorganisms that can fix atmospheric nitrogen. These can be both aerobes (*Azotobacter*) and anaerobes (*Bac. amylobacter*, *Clostridium pasteurianum*). Nitrogen fixation is a very important process since it enriches the environment with nitrogen. The conversion of nitrogen-containing compounds by microorganisms in natural conditions is shown in Fig. 11.19.

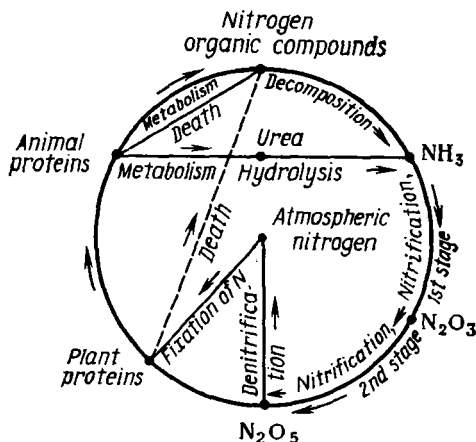


Fig. 11.19. Nitrogen circulation in nature

\* T. L. Simakova studied the Arctic soils to show that the nitrification process can proceed at temperatures below 0°C.

## 11.13. Ultramicrobes

Microorganisms that cannot be seen with the microscope are called *ultramicrobes*. Bacteriophages, filterable viruses and invisible forms of bacteria, are especially important ultramicroscopic forms for the practical life of man. For example, the size of dysentery bacteriophage is from 100 to 150 m $\mu$ . The size of the foot-and-mouth disease filterable virus is 8-20 m $\mu$ , of tobacco mosaic,  $12 \times 400$  m $\mu$ , and of encephalomyelitis, 70-100 m $\mu$ . Ultramicrobes can be seen only with the electron microscope (45,000  $\times$ ). Viruses (Fig. 11.20) are particles consisting of proteins and nucleic acid (DNA or RNA). They have no usual cell structure. Bacteriophages are also sub-cell organisms (Fig. 11.21). These are elongated formations with a thickened end\*.

In 1892, D. I. Ivanovsky studied mosaic disease in tobacco to discover that it is caused by filterable viruses, minutest microorganisms which easily pass the pores of biological filters impenetrable to visible (microscopic) bacteria.

Other filterable viruses were discovered later. They cause various diseases in man, animal and plants. For example, it was established that jaundice, rabies, smallpox, spindle-cell (chicken) sarcoma, encephalitis, and other diseases are caused by viruses.

The studies revealed physical and physiological characteristics of filterable viruses. If the preparation is kept in cold, the filterable virus preserves its activity for two years. It can move from cell to cell in an infected body. The action of chemical poisons on virus is different. For example, 50 per cent alcohol does not kill viruses at once. Viruses perish when exposed to the sun light. High temperature (about 90°C) kills them. Some viruses die at a temperature of 55°C. Drying does no harm to them, but on the contrary, it provides favourable conditions under which they can stand elevated temperatures. Viruses can change their properties and give them to their posterity.

The characteristic feature of pathogenic viruses is that they can grow and replicate only inside a living host cell. As a rule, they do not grow on artificial nutrient media. Hence they have no independent metabolism and use the enzymes of the living animal or plant cells.

The virus of mosaic disease is found in tobacco leaves as crystalline formations. Its crystalline nature has been proved by X-ray analysis. Crystalline viruses multiply very quickly. A virus introduced into a plant organism increases its number million times

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\* The thickened end of a bacteriophage, or its head, consists of a protein coat filled with DNA, while the thin end is a continuation of the proteinous head and is a tube.

during four weeks. The complicated chemical synthesis involves continuous mobilization of amino acids, nucleic acids, carbohydrates and lipoids from the protoplasm of a living cell to meet the demands of the growing crystalline virus. The process resembles crystallization from a saturated solution, but the plant leaves have no detectable amounts of these substances. This reproduction of a crystalline structure is only possible inside a living cell. An artificial nutrient medium and even triturated fresh tissues of the host plant fail to maintain the replication of the crystalline virus.

In 1899, N. F. Gamaleya showed that bacteria visible with the microscope are dissolved by the action of some invisible "creatures", or undergo *lysis*. Later it was found that the dissolution of bacteria was due to "bacteria eating", *bacteriophages*. \* For example, dysentery bacteriophage causes complete lysis in dysentery bacteria in 4-6 hours after its addition to the culture. The action of bacteriophages is specific.

The viability of bacteriophage is very high. When kept in the dark in a sealed tube it can remain alive for a few years. Bacteriophage stands the temperature of  $-190^{\circ}\text{C}$  but is destroyed at  $+100^{\circ}\text{C}$ . Ultraviolet rays kill it. Chemical poisons, such as ether, acetone, carbolic, oxalic and lactic acids, formaldehyde, glycerol and copper sulphate solution kill bacteriophages as they kill bacteria. Bacteriophages dissolving many pathogenic and saprophytic bacteria have

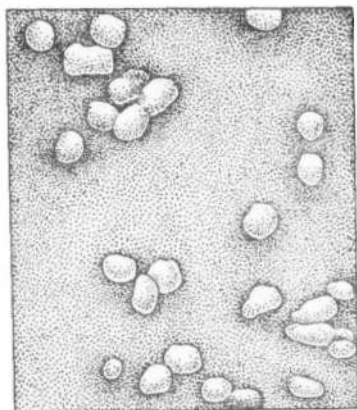


Fig. 11.20. Viruses

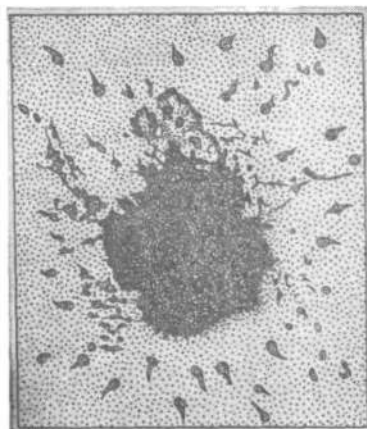


Fig. 11.21. First stage of an "attack" by a bacteriophage on bacteria (electron microscope picture)

\* The phage attaches itself to a bacterium with its tail process through which it releases its content. DNA of the phage alters the metabolism of the bacteria. The phage uses the enzymes of the bacterium in this process.

been studied. Some of them are used to control various pathogenic bacteria.

Bacteriophages and filterable viruses have no usual cell structure, hence an organized cell is not the last living unit.

Among ultramicrobes, there are organisms which are filterable forms of 'visible' bacteria. These forms can give, under favourable conditions, bacteria that can be seen with the microscope.

Filterable bacteria differ from filterable viruses in that they can grow on artificial media.

Ultramicrobes were first seen with the electron microscope which can be used to regard particles sizing  $0.005\ \mu$ . It is impossible to follow the vital processes of a living organism with the electron microscope since the current of electrons kills the living cell. But the electron microscope proves the existence of ultramicrobes.

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## 11.14. Algae, Fungi, Protozoa, Rotifers, Worms, and Myxobacteria

**Algae.** The term covers a great group of organisms which are lower plants, containing chlorophyll, having a primitive structure, without stalks, leaves or roots like in higher plants. The presence of chlorophyll colours algae green, but sometimes the colour is distorted by the presence in the cells of some additional pigments, such as blue phycocyanin, red phycoerythrin, orange carotene, and yellow xanthophyll. Depending on quantities of various pigments contained in algae their colour varies within a wide range.

Algae can be unicellular, multicellular formations and colonies. Some of them have cells deprived of any dense coats and have only a stronger external layer of protoplasm owing to which they can change their shapes. Cells of some algae have dense coats consisting mostly of cellulose. Pectins are often a component of the coat. The coat of some algae is strongly impregnated in lime or silica. Some cells have one or several nuclei while others have no typical nucleus, but only a coloured peripheral part and colourless centre in the protoplasm. Some algae contain pigments in special plasma bodies of various shapes, known as *chromatophores*. In most cases chromatophores comprise dense bodies, pyrenoids, rich in proteins. Starch, which is one of the assimilation products, is deposited round the pyrenoids. Fats, oil, leucosin, mannitol and glucose are also kept as nutrients.

Many unicellular, mainly motile forms, have a red spot and pulsating vacuoles.

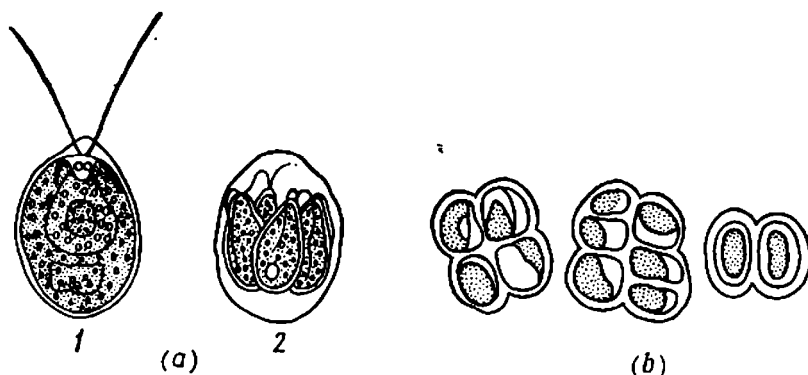


Fig. 11.22. Green algae (*Chlorophyceae*):

a—*Chlamydomonas* (1—vegetative species; 2—division into four cells); b—*Pleurococcus* (cells after division)

Algae are reproduced by vegetative, asexual, and sexual ways. In vegetative reproduction, a cell divides into halves in a longitudinal, transverse or oblique direction.

In asexual reproduction, the protoplast of a mother cell is divided into several parts which develop independently into full size cells.

The main habitat of algae are water bodies. Their growth is connected with the seasons of the year, availability of nourishment, and the salt composition of the medium. For example, various algae can live in one and the same water body at different times. Diatoms grow in winter and spring, while in summer greens and blue-greens develop in the same water body. In autumn diatoms grow again to inhibit the development of green and blue-green algae.

*Green algal* (*Chlorophyceae*, Fig. 11.22) are the most common type of algae. The cells of most green algae have a cellulose case, a vacuole with a cell juice, differentiated nucleus and chromatophores of cup-, band-, plate- or granular form. Green algae contain the same pigments as the higher plants, i.e. chlorophyll and carotene. They reproduce by sexual and asexual ways with formation of motile zoospores\*. The shapes of *Chlorophyceae* cells are varied. There are spherical, crescent-shaped, triangular, and irregular cells with various processes. Most *Chlorophyceae* are mononuclear.

The class of *Chlorophyceae* comprises protococcus (*Protococcineae*) algae. These are green unicellular organisms living single or in colonies, nonmotile when in the vegetative state. Some genera have constant number of cells. The product of assimilation is starch. The simplest representative of protococcus is *Chlorella vulgaris*.

\* Zoospores are parts of the cell after its division, provided with a flagellum. When the mother cell case is broken, zoospores are released into the surrounding medium and develop as independent cells.

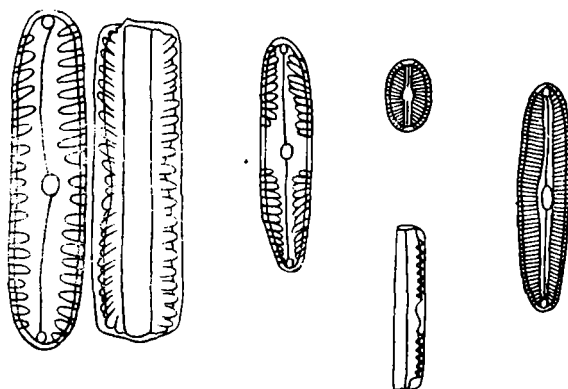


Fig. 11.23. Various soil diatomic algae *Navicula*

Green algae comprise also volvox organisms the greater part of which is covered with a case consisting of pectin and cellulose. Chromatophore is pure green, parietal, cup-shaped with a thickened base; it covers the lower part of the cell. Sometimes chlorophyll is masked with hematochrome and the algae are red, for example *Chlamydomonas nivalis* (Fig. 11.22a) which is found in polar regions (colours snow red). Cells are of various shapes: oval, pear-shaped, egg-shaped, spindle-shaped, etc. Two pulsating vacuoles are arranged at the flagella base. Volvox algae are widely spread. They are found in bodies of pure and dirty water, in fast and slow currents. They are often found in temporary water bodies, in various pits, pools and other depressions filled with rain water. They occur in soil. Part of them are saprophytic.

*Diatoms (Diatomeae, Fig. 11.23).* The case of diatomaceous algae consists of two overlapping shells. The shells are not closed and can be set apart. The protoplasm is arranged in thin layers by the walls to form a protoplasmic bridge inside many species. The rest of the cell space is filled with the juice. The nucleus is only one. Chromatophores\* are of various shapes: they can be granules, platelets, etc.

The products of assimilation are oil, volutin, and leucosin. The diatoms replicate either by vegetative division, or by auxo-spores. In the vegetative division, each part receives a mother shell, while the missing shell grows anew during the further growth of the cell.

Diatomaceous algae are widely spread in nature and propagate into large masses in fresh and salt water. The diatoms of the group *Pennales* occur mainly in the ground. They attach themselves to the substrate by gelatinous stalks or by a shell provided with a spine.

\* In addition to chlorophyll, chromatophores contain brown pigments and the algae are therefore yellowish or dark brown.

The diatoms are of great practical importance since they can be used as fodder.

**Blue-green algae (Cyanophyceae, Fig. 11.24).** These are uni- or multicellular organisms with a characteristic structure of their cells. They have no typical nucleus or chromatophores. The protoplast of blue-greens is differentiated into peripherally coloured layer (chromatoplasm) and the central part (centroplasm). The assimilating pigments are chlorophyll, phycoerythrin, phycocyanin, and carotene. Depressions contain special bodies, endoplasts, of dense or viscid consistency. The "chromatin substance", stainable with nucleus dyes, is found between endoplasts of the plasmic walls.

The cells of blue-green algae miss vacuoles with cell juice. Therefore, the cell fully shrinks during plasmolysis. The cells of these organisms have gas vacuoles. Their density is lower than of water and the organisms therefore float to the surface. The cells of blue-green algae are coated. The coat can be thin and slightly visible. or it can be thick. The coats are often covered with mucilage which promotes formation of colonies. The coats are mainly of pectin. In filamentous algae, a series of cells is enclosed in a cylindrical hollow case. The structure consisting of cells enclosed in a case makes a thread, or filament.

Blue-green algae are widely spread in nature. They grow in both fresh and salt water, in soils, on rock, in the Arctic and in deserts. This is due to their extraordinary stability to unfavourable conditions and to inexacting requirements for nutrition.

**Fungi\*.** These have no chlorophyll and do not therefore need sun light. Fungi, which grow predominantly in filaments (mycelium) are called molds. Mold is a branching growth resembling hair, threads, or hyphae, which form wooly patches visible to an unaided eye, known as mycelium. Those fungi which develop predominantly in the form of unicellular elements, are called yeast. It is impossible to draw a distinct line between mold and yeast. Some of them can grow as yeast-like cells, and some in the form of filaments to form mycelium. This depends on the environmental conditions. For

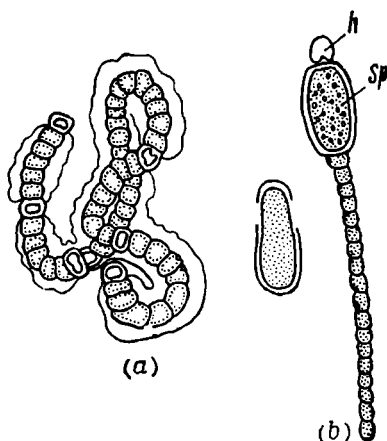


Fig. 11.24. Blue-green algae (Cyanophyceae):

a—*Nostoc commune*; b—*Anabena*; h—heterocyst; sp—spore; spore germination (left)

\* Fungi grow in soil, on plants, animals, and on structures of sewage systems.

example, molds grow at low temperatures, while the presence of some nutrients (such as blood, glucose, compounds, containing the —SH group) and the absence of oxygen (anaerobiosis) are favourable for the development of yeast-like cells. There exist various substances (fusel oils, cobalt ions, camphor, etc.) which promote the transition from the yeast-like form to the filaments.

Yeast and molds differ from the lowest order organisms by the presence of a solid shell (it consists of cellulose in yeast and of chitin, or like substances, in molds), by the method of taking up nutrition, by the absence of organs of locomotion, by the vegetative method of growth (the growth is continuous, irrespective of the size), and by specific morphology.

Yeast and molds have a high enzymatic activity and are used in industry and sanitation. Some types of yeast grow to give valuable products, such as alcohol, acetones, etc., while others destroy organic matter of vegetable and animal remnants. Molds are used to produce antibiotics.

**Protozoa.** These are unicellular animal organisms. Most of them are hundreds of times greater than bacteria. Like animals they have no solid case, but have a soft and flexible, and relatively brittle outer cell membrane. Usually it consists of chitin or like compounds and does not contain cellulose.

Inside the case there are a nucleus and cytoplasm. The cytoplasm contains vacuoles which perform various functions. For example, the food vacuole performs the role of a stomach. Dissolved nutrients pass from it into the cytoplasm and consumed by the organism in its vital processes. Other vacuoles accumulate metabolites which are then excreted. The cytoplasm contains also granules holding nutrients which are used whenever the organism lacks them.

Protozoa breathe with oxygen dissolved in water. Harmful substances (carbon dioxide, etc.) are discarded from the organism through the entire surface and through a contractile vacuole.

Protozoa have no strictly differentiated organs, but they are sensitive to heat, light, various chemical actions, and also to the gravity force and electricity. Most protozoa are holozoic.\* When they take in dense particles of food they digest them into soluble substances by which the cell, or the cells of the organism obtain the required nutrition.

Protozoa are reproduced by binary division. Mastigophora (the protozoa having flagella) are divided by their longitudinal axis, while infusoria (those having cilia) undergo transverse division. Each division has the full set of physiological properties and genetic potentialities of the parent cell. Some protozoa replicate sexually.

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\* Like animals, they consume only soluble substances. [(Plants are holophytic.)]

When in unfavourable conditions, some protozoa turn into *cysts* with a dense case which protects them from the harmful actions of the environment. Cysts can live in the absence of moisture for several years. When ponds or rivers get dried up, cysts are carried by wind into various directions to infect the soil and open water bodies. For example, the cysts of dysentery and intestinal ameba can live in water and other environmental objects for 3 or 4 months.

There are pathogenic microorganisms among protozoa. These are causative agents of malaria, amebic dysentery, and other diseases.

Activated sludge and biological film can contain representatives of *Sarcodina*, colourless *Flagellata*, ciliated infusoria (*Ciliata*), and sucking infusoria (*Suctoria*).

*Sarcodina* (Fig. 11.25). Common ameba is a representative of this class. It occurs in dirty water, on the bottom or in silt. This is a colourless jelly constantly changing its shape. The body of the ameba consists of a semiliquid cytoplasm with a small bubble-shaped nucleus. There are processes of protoplasm by the circumference of the body, called pseudopodia, by which ameba moves about and also absorbs nourishment (bacteria, algae, protozoa). The food is digested in the food vacuole, then transferred into the cytoplasm, where it is utilized for the building up of the cell. The metabolites and excess moisture are excreted from the organism through the entire surface of the body and also through the contractile vacuole. Amebas reproduce themselves by division. They also form cysts.

*Mastigophora*. This class includes colourless infusoria provided with flagella (*Flagellata*) and coloured forms, e.g. *Euglena*. The shape of the body in *Flagellata* is more or less constant. Their food is bacteria. They replicate by binary division. Develop in the presence of sufficient amounts of organic matter and bacteria.

Representatives of this group have either one (*Oicomonas*, Fig. 11.26a), two (*Bodo*, Fig. 11.26b), or many (*Trepomonas*, Fig. 11.26c) flagella at the front end of their bodies which are protoplasmic filaments. Flagella are the locomotor organs. *Oicomonas* cells have a depression at its one end, which resembles lips. The other end of the cell has a pedicle by which it attaches itself to a solid object. The flagellum is in constant vibration by which the cell is propelled. Attached cells use the flagella to catch food which enters them with water through its front end.

*Bodo* cells move about by means of two flagella, one of which is directed forward and the other backward. The second flagellum performs the function of a rudder or a stack by which the cell attaches itself to a solid object.

*Trepomonas* have a wave-shaped flattened body. Each end of the cell has a mouth with four flagella. The cell contains two oblong nuclei and one contractile vacuole.

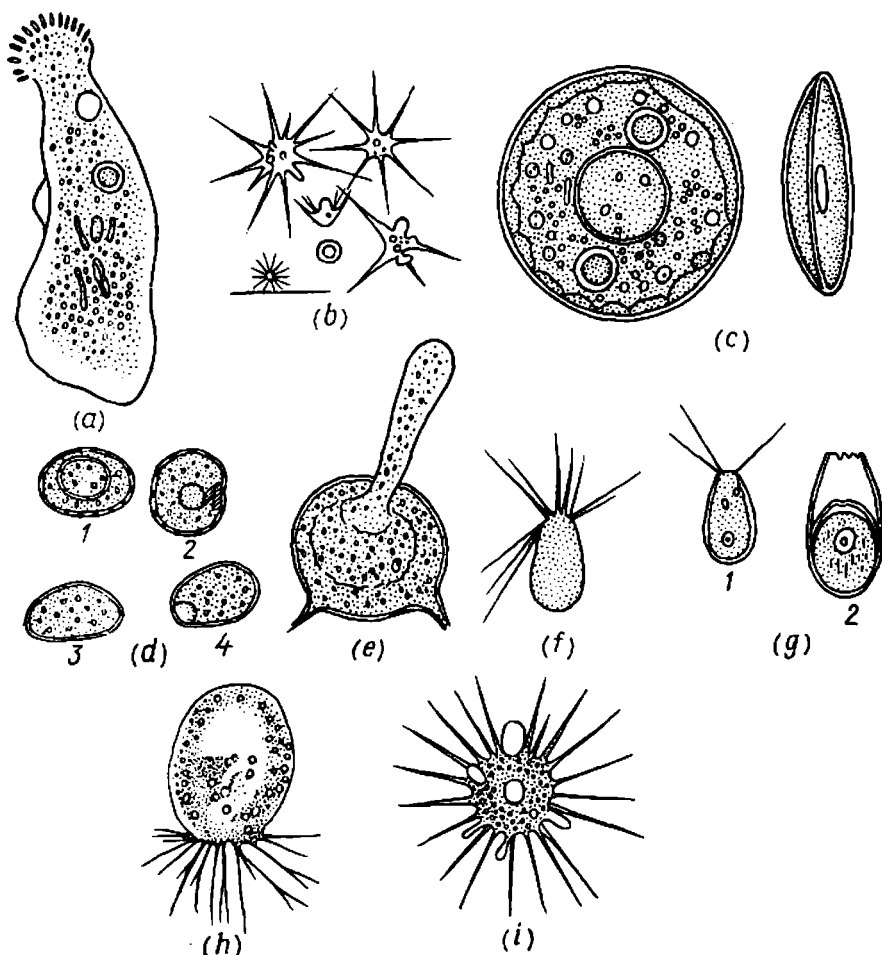


Fig. 11.25. Protozoa (*Sarcodina*):

a—*Amoeba lixax*; b—*Amoeba radiosa* (various stages); c—*Arcella discoides*; d—*Centropyxis laevigata* (1—shells with a cyst; 2—shell with a mouth; 3—front view; 4—side view); e—*Centropyxis aculeata*; f—*Euglypha alveclava*; g—*Euglypha laevis* (1—shell with pseudopods; 2—shell with a cyst); h—*Pamphagus hyalinus*; i—*Aktinophrys vesiculata*

Like a common ameba, *Euglena* green is found in stagnant pools. Its body is elongated. The outer cytoplasm layer is dense and the cell almost does not change its shape as it moves. *Euglena* can contract slightly to become shorter and wider. The front end of *Euglena* bears a cytoplasmic process, the flagellum, by which it moves about.

The cytoplasm of *Euglena* contains a nucleus and many (over twenty) green oval chloroplasts which give it green colour. Chloroplasts contain chlorophyll by which the organism photosynthesizes

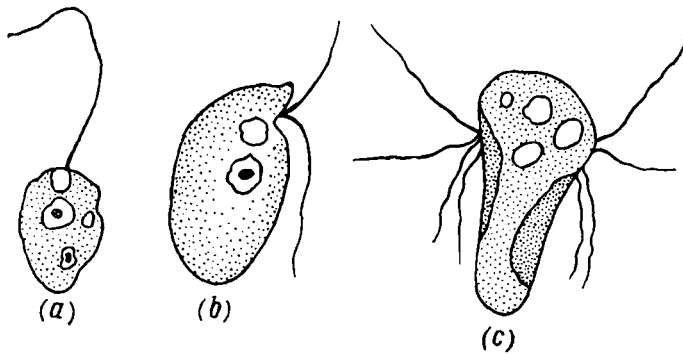


Fig. 11.26. Protozoa (*Flagellata*):

a—*Oicomonas socialis*; b—*Bodo*; c—*Trepomonas steini*

the cell substance (like plant). But chlorophyll disappears when *Euglena* gets in the dark. In new conditions it assimilates dissolved organic nourishment. Hence, when in the light, *Euglena* has the signs of a plant, and in the dark, the signs of an animal. The metabolites and excess water are withdrawn from the body through a contractile vacuole. *Euglena* replicates by simple division. It can form cysts.

*Ciliata*. This is the class of organisms provided with cilia (Fig. 11.27). Ciliated infusoria are characterized by a great variety of shapes, different arrangement and different number of cilia, by the method of taking food, and the mode of life. There are over 3000 species of infusoria. Their food is mostly bacteria, small algae, other protozoa, infusoria included. Many infusoria are parasites. Their usual hosts are man, animal, fish.

The body of protozoa consists of one cell, but its structure is complicated, like for example in *Paramecium caudatum* (Fig. 11.27a) which lives in sewage. *Paramecium* has a constant shape because its outer cytoplasm layer is dense (chitin shell). The entire body of *Paramecium* is covered with longitudinal rows of fine cilia. By wave-like movements of its cilia, *Paramecium* moves in the surrounding medium. One end of the body has a mouth with a short tubular throat into which food is pushed by larger cilia located around the mouth. From the throat food is delivered into the food vacuole where it is digested and the nutrients are taken up by the body. Nondigested food is excreted through the anal pore. The contractile vacuoles, located in the cytoplasm, collect the metabolites and discard them. *Paramecia* are reproduced by simple division and by sexual multiplication.

There are sucking infusoria (*Suctoria*, Fig. 11.28) which do not move in the environment but attach themselves to plants, molluscs, sludge flocs, by a noncontractile stalk. Their body is coated in a

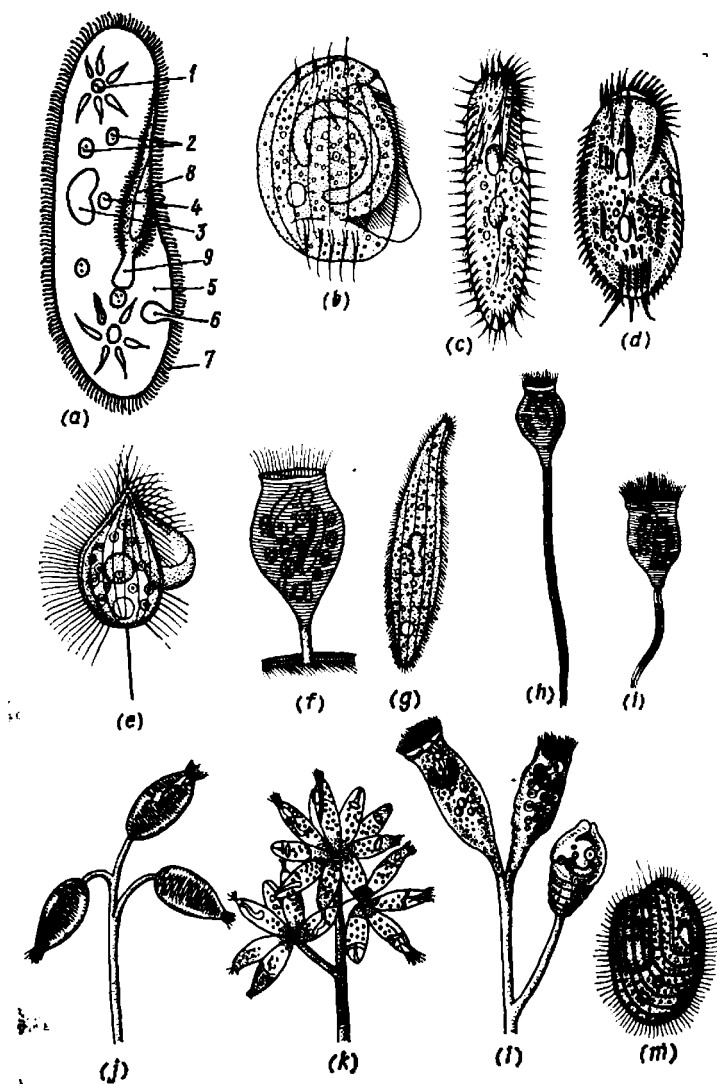


Fig. 11.27. Infusoria (Ciliata):

a—*Paramaecium caudatum* (1—contractile vacuole; 2—food vacuole; 3—bigger nucleus; 4—smaller nucleus; 5—cytoplasm; 6—excrement outlet; 7—cilia; 8—mouth; 9—throat); b—*Aspidisca costata*; c—*Oxytricha pellionella*; d—*Stylonychia pustulata*; e—*Cyclidium glauc coma*; f—*Rhabdostyla ovum*; g—*Lionotus lamella*; h—*Vorticella microstoma*; i—*Vorticella convallaria*; j—*Opercularia coarctata*; k—*Opercularia glomerata*; l—*Epistylis plicatilis*; m—*Cinetochilum margaritaceum*

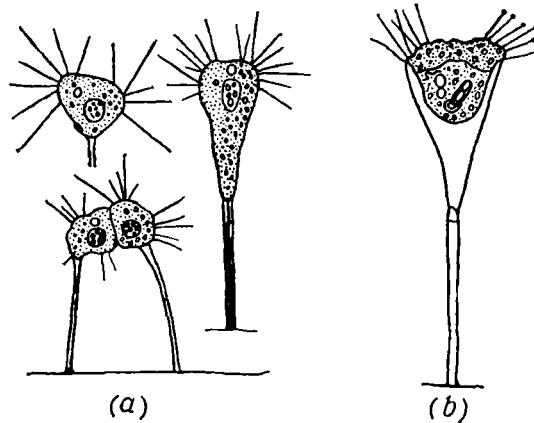


Fig. 11.28. Sucking infusoria (*Suctoria*):  
 a—*Tokophrya lemnaeum*; b—*Acineta flava*

pellicle. Many of them form dense skinny enclosures. In some infusoria the upper end remains free while in others it grows into the upper part of the body. The reproduction of infusoria is by budding, and in rare cases by division. Suctoria have no mouth, but have tentacles, fine tubes open at their ends. The channel of the tube leads deep into the body. The upper end of the tentacle is either thickened like a sucker, or sharpened. The tentacles are either spread over the entire body or arranged in bundles. The strength of the tentacles is so great that small suctoria can hold simultaneously several ciliated infusoria, each of which sometimes exceeds the size of the infusoria of prey. Using its tentacles the suctoria suck in the liquid constituent of the prey body. Suctoria feed mainly upon ciliated infusoria, but sometimes use also algae, various animals, and vegetable remnants.

There is a species of infusoria called *sedimentators* because they take food by sedimentation of suspension. These organisms have a mouth located in a depression into which suspension taken with water is sedimented. The infusoria have complicated cilia by which they manipulate foods, sort them out by size, shape and type. The cilia are the same locomotor organella but modified to catch food.

Protozoa occur everywhere, in sewage, sludge, excrements, soils, dust, water of rivers, ponds, lakes, oceans, aerobic sewage treatment plants. Protozoa are active participants in mineralization of organic substances in natural and artificial conditions of sewage treatment. But it should always be remembered that some protozoa are causative agents of many diseases in man and animal.

**Rotifers** (*Rotatoria*, Fig. 11.29). *Rotatoria* are representatives of the animal kingdom and have more complicated structure than protozoa.

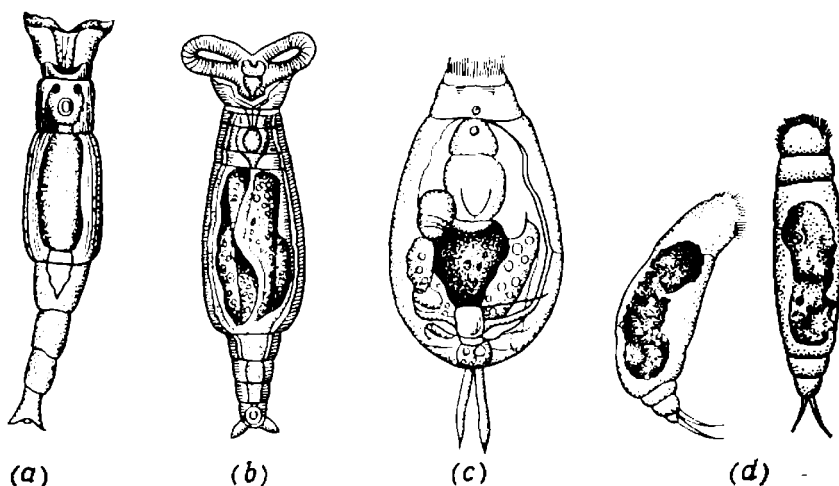


Fig. 11.29. Rotifers:

a—*Philodina roseola*; b—*Callidina vorax*; c—*Cathypna luna*; d—*Notommata ansata*

Rotifers are coated with a translucent but strong testa (shells) which ends in its upper end with six regular and symmetrical processes on the back and two on the abdomen. The wider anterior opening in the testa has the head crowned with a rotary apparatus, whose cilia are set in constant motion. On its bottom the testa ends with a narrow opening from which emerges a pedicle, a muscular growth with a segmented chitin shell. The pedicle ends with two fingers with glands at their base to secrete sticky substance by which the rotifer can attach itself to a substrate.

The digestion system consists of a mouth which widens to a muscular throat, a masticatory apparatus intended to grind food, an esophagus, and a stomach. The stomach leads to a narrow intestine connected with the excretory organ.

The blood supply and respiratory systems are absent in rotifers.

By the method of taking food the rotifers are sedimentators. Using their cilia, the attached organisms give a spindle-like movement to water whose funnel is directed into the mouth of the animal with its narrow end. Protozoa, bacteria and organic substances get into the rotifer through this "funnel". Most rotifers have eyes (red spots).

Rotifers are aerobes and are sensitive to oxygen deficiency. The highest temperature that *Rotatoria* can stand is 50°C. When the conditions worsen, the rotifers form a cyst (the head and the leg being pulled into the testa). Rotifers are sensitive to the changes in the active reaction of the medium, and are indicator-organisms characterizing the efficiency of the aerobic sewage treatment plant in work.

**Worms (*Vermes*).** To characterize mineralization of organic substances in natural and artificial conditions, the investigators give special attention to round (*Nematodes*) (Fig. 11.30) and oligochaetous worms.

Roundworms (*Nematodes*) have a round, thread-like body devoid of any segmentation, normally narrowed at both ends. These are primitively organized animals without blood-vascular or respiratory systems.

The alimentary system is tubular, consisting of a muscular esophagus and an intestine passing through the entire body. Food is taken through the mouth located in the centre of the head end of the body. There are several mobile lips around the mouth. These are provided with papillae and bristles. The excretory function is performed by a special cell which opens outside through a special pore, normally located in the region of the esophagus or in the end of the body.

The outer coverage of the nematode body consists of two tightly connected layers. The upper layer, the cuticle, is a translucent, colourless, very solid substance almost impermeable to extraneous matter. For this reasons, some *Nematodes* can stay for a long time in unfavourable conditions. The lower layer, subcuticle, consists of fine-grain thick translucent protoplasm (hypoderm). It has no cell structure, but the nuclei are preserved. *Nematodes* are reproduced sexually, by laying eggs. Sometimes, freshly laid eggs contain formed germs inside them. Freely living forms have scores of eggs, while their number in parasitizing worms is millions. The life cycle continues for 5-6 days in some species, and in others it continues for a month and over. The development is promoted by favourable temperature conditions.

*Nematodes* have a nerve ring around the esophagus. The sensing organs in roundworms are in the form of little eyespots. The eyespots serve to perceive light and are present only in the free-living forms. They are absent in parasites. The depressions on the head sides are connected with the nerve ring and are an organ of chemical sensing.

*Nematodes* are widely spread in nature. They occur in sea and fresh water, in soil, on plants, they parasitize on man and animals.

Free living aqueous *nematodes* are mostly benthonic organisms closely connected with the underground vegetation or ground. Many *nematodes* live on piers, docks, buoys, etc. The presence of *nematodes* in the plankton and in the ice is only occasional.

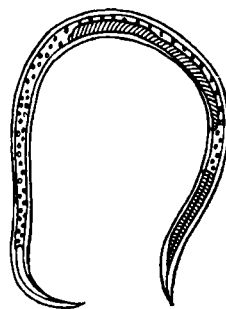


Fig. 11.30. *Nematoda* (roundworms)

Nematodes are characteristic representatives of active film on biological oxidizers, sewage treatment plants.

*Oligochaetae* consist of segments. Their bodies are provided with bristle which can be in the form of needles, hairs, and tooth-like formations. Some oligochaetae have branchial appendages. In the absence of branchia, they breathe through the skin.

The inner structure of segmented worms (Annelida) is repeated in each segment. The organs are either repeated in each segment or narrowed as they pass from one segment into another (intestine, skin, nerve system); or they can form appendages (blood-vascular and nerve systems).

Oligochaetae can reproduce by sexual way and by division (each divided part regenerates to the full size).

*Aelosoma* and *Nais* are the oligochaetae which dwell on artificial biological oxidizers. *Aelosoma* have bristle bundles arranged in different directions. The skin inclusions are from red to milk-white. The reproduction is mainly asexual.

*Nais* usually have bristles split into rudimentary teeth at the outer end, and the bristles are only sharpened in a few species. The eyes are sometimes absent.

Sludge particles are the source of nourishment for worms. They are passed through their bodies, mineralized, and the residues are discharged into the surrounding medium in the form of enlarged particles. This promotes clarification of the treated liquids. The presence of large number of worms indicates excess silting of the filter.

**Lower Crustaceans.** These are fresh-water dwelling organisms. *Cyclopes* and *Daphnia* are representatives of these cancroids. *Cyclopes* move about by the agency of legs located on the animal chest, while *Daphnia* move by their antennae supplied with propelling bristles.

Lower crustaceans are active filtering organisms. They pass large amounts of water through their bodies to retain suspended matter. Part of this matter is mineralized while the rest is discarded from their body in the form of compact (glued) aggregations. They feed on bacteria, small algae, organic suspended matter. Crustaceans themselves are food for fish. Lower crustaceans can be carriers of larvae of parasitic worms; for example, *Cyclopes* filter water to swallow the larvae of tape worm parasitizing on man and animal. When a larva gets into a fish it begins growing, and if a man takes this fish without sufficient boiling, he gets infected with the larvae, which develop into a grown-up worm reaching 17 metres in length. A man can be infected with several worms simultaneously since one fish can bear to 2000 larvae.

**Myxobacteria.** These bacteria are much like protozoa and resemble blue-green algae.

Myxobacteria are close to true bacteria. They are the same small and rod-shaped. They multiply by transverse isomorphic fission;

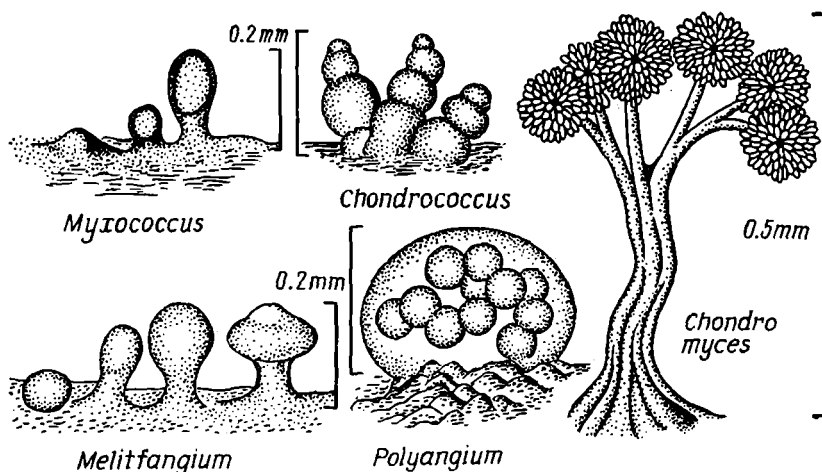


Fig. 11.31. Fruit-shaped processes of some myxobacteria

they are chemosynthesizing, heterotrophic organisms; can grow on artificial media. Most of them are only aerobes, nonsporeforming mesophiles, developing at neutral reaction of the medium (pH 7.2).

At the same time, myxobacteria differ significantly from true bacteria by the absence of solid shell, by the ability to move by actively bending their bodies (they have no flagellae), and by that they can form flat formations.

Myxobacteria are similar to some protozoa in that they can form fruit-bearing bodies which are a variation of the colony. During their multiplication, these organisms excrete a gelatinous substance into the surrounding medium in which they live. When the gelatinous substance dries up, it forms a kind of a case inside which the cell rests. In some species, the gelatinous substance envelops aggregations of cells to form cysts which look like fruits. Figure 11.31 shows these formations of some myxobacteria. Each tubercle contains a multitude of cells which do not perish when dried up and can stand other unfavourable actions. After a period of rest, when moisture is available, the cyst softens and the vegetative cells are released to the environment.

Myxobacteria live on felled trees, dead foliage, seaweeds, manure, etc. Some species are pathogenic for aquatic fauna.

Myxobacteria actively destroy dead organic matter, such as cellulose and chitin, and also various animal and vegetable materials.

Myxobacteria do useful sanitary work: they destroy wastes and turn them into compounds that can be used as nourishment for plants.

## 11.15. Effects of Environments on Growth of Microorganisms

Microorganisms are found everywhere provided the conditions permit. These conditions are (1) sufficient moisture; (2) nourishment; (3) and suitable temperature at which the vital processes can occur. Hence the existence of microbes depends on the environmental factors which are called ecological factors. These include temperature, illumination, elements of nutrition, organogens (C, N, P, S, H, O), the salt composition of the medium, osmotic pressure, surface tension, and active reaction of the medium.

Microorganisms adapt themselves to the environment and any deviation from the optimum conditions inhibits their growth and even kills them. Detrimental factors are the change in the pH of the medium, disordered oxygen conditions, sharp temperature changes, depletion of nourishment, action of direct sun rays, and also biological factors. For example, microorganisms are killed by lysis (dissolution of their cells in bacteriophages) and by the antagonistic action of other bacteria.

**Growth Factors.** Some microorganisms cannot synthesize sufficient quantities of organic substances (amino acids, purine and pyrimidine bases, vitamins) required for the construction of new cell material. The lacking substances should therefore be added to the medium where the microorganism grows. These substances are known as *growth factors*. A microorganism which lacks a certain growth factor is called *auxotrophic* with respect to the lacking compound, while a microorganism which does not require this compound is called *prototrophic*.

The microorganism requirements for growth factors are not constant and can change depending on the cultivating conditions. For example, the mold *Mucorrouzii* requires vitamins biotin and thiamine only when it grows in anaerobic conditions, while it synthesizes these vitamins itself when grown in aerobic conditions. This flexible attitude to the growth factors is found in organisms which can grow on media with varying pH. The increase in the temperature over the optimum changes the attitude of microorganisms to growth factors.

Microorganisms can be auxotrophic towards one or more of the twenty amino acids which are parts of protein. Amino acids are often replaced by peptides with low molecular mass. Peptides act like an effective transport of amino acid into the microorganism cell.

Some microorganisms (bacteria and protozoa) require purine and pyrimidine which are components of nucleic acids. Microorganisms, which do not synthesize purines and pyrimidines and cannot include them into the composition of nucleotides, require nucleotides.

Most readily available sources of carbon, hydrogen and oxygen are organic compounds; carbohydrates, amino acids, polyhydric alcohols, lipids, and salts of fatty acids. Hydrocarbons are utilized by only a limited number of microorganisms.

The ability to consume aromatic compounds is best of all inherent in pseudomonads. These substances are split in aerobic conditions. In order to synthesize amino acids (and proteins), purine and pyrimidine bases, and also some vitamins, the microorganism should get nitrogen in a suitable form.

Nitrate ion  $\text{NO}_3^-$  is the source of nitrogen for many algae, fungi and actinomycetes. If the medium contains insufficient amounts of nitrogen-containing compounds, some microorganisms can fix nitrogen from the air.

Organic compounds can be used as the source of nitrogen only by those microorganisms which can split them with liberation of ammonia.

Microorganisms require, for their growth, mineral phosphates as acid salts,  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$ . These salts also control the pH of the medium (buffer action of the solution). Living cells contain phosphorus as phosphates, mainly those of sugars in nucleotides and nucleic acids. Since DNA, RNA and ATP, the important components of the living cell, contain phosphates, this proves their importance for the vital processes of a cell. Nucleic acids are the sources of phosphates in natural media (broths, for example).

Sulphur, like phosphorus and nitrogen, is also a component of protein of a living cell, and it is therefore absolutely necessary for the synthesis of cell material. The amino acid cystine, which is a component part of protein, is the most important sulphur-containing component of the cell. Sulphur is present in cystine in the thiol group ( $-\text{SH}$ ). Methionine, biotin, thiamine, glutathione, etc., are cystine derivatives. The source of sulphur for many microorganisms are the sulphate ion  $-\text{SO}_4^{2-}$ , and thiosulphate ion  $-\text{S}_2\text{O}_3^{2-}$ . Microorganisms reduce sulphur to  $\text{S}^{2-}$ . Some microorganisms do not reduce sulphates and require reduced sulphur (e.g. hydrogen sulphide and cysteine).

**Effect of Temperature.** Most microbes live at temperatures in the range from 0 to  $80^\circ\text{C}$ , and for the vast majority of them the most suitable temperature is from 3 to  $45^\circ\text{C}$ . (Microbes were recently discovered which can stand the temperature over  $100^\circ\text{C}$ .) All microorganisms can be divided into three groups by their attitude to temperature:

- (1) psychrophilic (fond of cold) bacteria; these develop best at temperatures close to zero;
- (2) mesophilic bacteria, developing at moderate temperatures from  $5$  to  $40^\circ\text{C}$  (optimum temperatures,  $32$ - $35^\circ\text{C}$ ); and
- (3) thermophilic bacteria, for which the minimum admissible

temperature is 40 and the maximum 80°C, the optimum temperature being about 55°C.

The intensity of biochemical processes (like that of chemical ones) directly depends on the temperature. If the temperature increases 10°C, the velocity of biochemical processes increases two or three times. But unlike chemical processes, biological processes require very slow change in the temperature so that the living organisms could adapt themselves to the changed conditions. Sharp temperature drops are detrimental and can kill useful microorganisms. Many microbes pass into the state of 'latent' life when cooled to low temperatures. This state is called anabiosis. Chilled organisms can revive when warmed up. Microbes can stand the temperature of -190°C, but periodic frosting-defrosting is detrimental to them. Normally, high temperature kills the greater part of microbes. Bacterial spores are killed at a temperature of 120°C and a pressure of 1.5 atm when kept in these conditions for 20-40 minutes.

Any change in the temperature decreases the activity of the microbes, which is then slowly restored. High temperature kills microorganisms by destroying RNA and by injuring the cytoplasmic membrane.

Intermittent frosting kills microorganisms by the conversion of the liquid medium into ice and by the loss of water from the cell.

**Effect of Light.** The sensitivity of various microorganisms to light is different. For algae, purple and green bacteria, which synthesize organic matter by assimilating carbon dioxide, light is the main condition of their existence.

The flora of the surface water is known to utilize CO<sub>2</sub> as the source of carbon in photosynthesis and to liberate oxygen into the environment. Light is therefore very important for the oxidation processes.

Light is however detrimental to pathogenic microflora. Ultraviolet radiation kills bacteria by intensifying their oxidation processes. This phenomenon can be compared with fading of dyes in the light. Light is believed to act on the cytoplasm of bacteria to induce photochemical processes in it which, after all, causes their death. Most saprophytic bacteria are insensitive toward stray light.

**Effect of pH of the Medium.** Each species of microorganism can live only in its special medium. The effect of pH on the activity of microorganisms is due to the action of hydrogen ion on the enzymes of the cytoplasmic membrane and of the cell wall. The changing hydrogen ion concentration in the medium does not change its concentration in the cytoplasm because the membrane is impermeable to the hydrogen ion and the hydroxyl ion.

Hence the changing pH interferes with the catalytic activity of ecto-enzymes and enzymes in the cytoplasmic membrane and the cell wall.

Optimum pH for most bacteria is about 7.0. But some microbes can stand the variations in the pH:

Optimum pH for Various Bacteria	
<i>Escherichia coli</i> . . . . .	4.4-7.8
Nitrite bacteria . . . . .	4.8-8.8
Nitrate bacteria . . . . .	6.5-9.3
Sulphur bacteria . . . . .	1.0-4.0

The optimum pH for pathogenic bacteria parasitizing on animals is from 7.2 to 7.4. Molds and yeast grow better in an acid medium (pH 4-6), while actinomycetes, on the whole, prefer weak alkaline media.

The value of the pH is important for the growth and the morphology of microorganisms. It follows, therefore, that when cultivating the required microflora, special attention should be given to pH of the medium.

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## 11.16. Bacteriological Analysis.

### Isolation of Pure Culture

A sample of water intended for bacteriological analysis should be taken in sterile vessels and analyzed as soon as possible in order to prevent changes in the bacteriological population in the sample due to bacterial propagation and destruction.

A sample of water for bacteriological analysis taken from natural basins should be 20-25 ml. Samples of artesian or tap water should be bigger, from 1 to 7 litres, and of sewage, only 1 ml.

The main requirement for the bacteriological equipment and procedures is sterility, i.e. glassware should not contain a single living cell.

Most nutrient media are sterilized in autoclaves by heating to 120°C for 30-45 minutes, or at 100°C for three days, in 30-45 minute daily sessions (fractional sterilization). By the time of the second heating, the spores develop into adult forms which are more easily destroyed during the second procedure. Thermostable bacteria require the third heating.

Glassware for bacteriological analysis should be sterilized in a drying cabinet at a temperature of 160°C for two hours or in an autoclave at a temperature of 120°C and a pressure of 1.5 atm. Other objects should be sterilized in the flame of a spirit burner.

The total number of bacteria is determined by counting colonies\* on meat-peptone agar after cultivation for 48 hours at 20-22°C.

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\* A colony is a collection of bacteria, or the posterity of one bacterial cell.

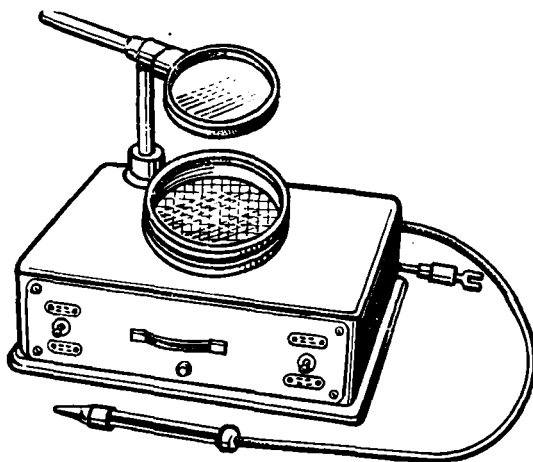


Fig. 11.32. Colony counter

The number of colonies grown on a solid medium is counted through a lens magnifying not less than 5 times. A special instrument, shown in Fig. 11.32, is now used to count colonies in Petri dishes. A dish is overturned on a special device and illuminated from below. A lens fixed above the Petri dish is used for counting the colonies. The result is multiplied by the dilution factor to determine the number of bacteria in a litre of the sampled water.

Bacteria can be counted straight under a microscope. A drop of test water is spread over a known surface area of a defatted glass. The smear is dried up in the air, fixed with alcohol or in the flame of an alcohol burner, and stained\* with a 1 per cent solution of erythrosine in a 5 per cent solution of carbolic acid water. From 20 to 40 fields of vision are counted and a mean found.

Pure water is filtered through membrane filters of nitrocellulose which retain bacteria from the water. The bacteria are then treated on the object glass. The results of the direct bacteria counting are

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\* Gram's staining method is used in the study of unknown bacteria. The method consists in staining microorganisms with methyl violet followed by subsequent treatment with iodine. Thus stained bacteria, which do not lose crystal violet under the action of alcohol, are said to be *gram-positive*, while those decolorized by alcohol are called *gram-negative*. The differential staining depends on the properties of the cell case and the cytoplasmic membrane. The stain and iodine penetrate inside all cells, but gram-positive cells form a more stable coloured compound than gram-negative cells do. These microorganisms have significant differences, for example, the RNA to DNA ratio is 8 : 1 in gram-positive and 1 : 1 in gram-negative microorganisms, the fat content is low in the former and high in the latter cells. In addition to differential staining, unknown microorganisms are examined for their morphological, biochemical and other properties.

exaggerated compared with the counting of colonies since both live and dead bacteria are counted in the direct method, while only live bacteria are counted in colonies.

By *pure culture* is meant a culture of a species obtained by cultivating one cell.

Pure culture of a given bacterium can be prepared by two methods: (1) by dilution with sterile physiological saline solution until one millilitre contains only one cell which is transferred onto nutrient medium to cultivate pure culture of a given species; (2) by isolation of bacteria of solid nutrient media (for example, on agar-agar).

A pure culture is prepared by multiple reinoculations. An inoculated liquid medium (warm agar-agar) is placed in Petri dishes and allowed to congeal in a thin layer. The bacteria are thus fixed on the surface or inside the gel. Colonies of bacteria grow in 24-48 hours. They have specific shapes, structure, or colour. The colonies are isolated and used to inoculate new portions of the medium.

There are bacteria with specific physiological properties which require special methods for isolation of pure culture. These are nitrifying bacteria, iron bacteria, inducers of methane fermentation, etc. Elective medium are used for growing pure cultures of these microbes.

Elective media (according to Vinogradsky) provide favourable conditions for the growth of certain species. This method requires much time to isolate the culture. For example, about 60 days are required to isolate cellulose-fermenting bacteria.

To intensify this process, A. A. Imshenetsky suggested that special optimum media, which would provide conditions for the growth of the main species and its companions, should be used. One species never develops in isolated conditions in nature. The process is always symbiotic. For example, the bacteria decomposing cellulose better develop in the presence of symbiotic companions which consume the products of cellulose decomposition (glucose, alcohol, organic acids). The decreasing content of these substances in the medium promotes rapid multiplication of cellulose bacteria. The use of optimum media therefore considerably shortens the time of isolation of a given species of bacteria.

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## 11.17. Main Ways of Infection Spreading

*Infection* is the interaction of pathogenic microbes with a macro-organism under certain conditions of the environment, which can cause an infectious disease in this organism. (Pathogenicity is the potential ability of some microorganisms to cause the infectious process.) Pathogenic microbes are characterized by specificity, i.e. each microorganism can induce a definite infectious process. But the development of a pathogenic process, its character, gravity, duration, and the outcome depend largely on the reactivity and resistance to infection of man or animal. Pathogenic microbes can be found in healthy persons without any pathological effect on them. It has been proved that inadequate nourishment, cold, alcohol, physical fatigue, etc. promote the development of infections.

Many pathogenic microorganisms produce enzymes capable of destroying tissues and cells of a living organism to increase the danger of bacterial penetration into the attacked body.

The most important characteristic of a pathogenic microbe is its toxicity. Exotoxins and endotoxins are distinguished. Exotoxins are poisons which easily diffuse in the surrounding medium, while endotoxins are present only in the bacterial cell and are released only after its death. The action of exotoxins is specific, i.e. they affect only certain tissues. For example, tetanus exotoxin affects the nerve system to cause spasm of the muscles, the diphtheria exotoxin attacks the cardiovascular system, the adrenal glands, etc. Microbial exotoxins are strong poisons which endanger life even in small concentration, while endotoxins are less toxic and not so specific in their action; they cause general signs of poisoning, such as headache, weakness, dyspnea, etc. Endotoxins consist of polysaccharides and lipoproteids, while exotoxins are protein in nature.

Epidemic diseases can spread on the condition that all three links of the epidemic chain are involved: the source of infection, ways of its transmission, and susceptibility of the population of this disease. An affected man or animal, or carriers of bacilli can be the source of infection. A carrier can be a practically healthy organism to whom the parasitic microbes do no harm but only grow in it and are released into the surrounding medium. Hence a bacilli-carrier is a permanent source of spreading the infection.

Infectious diseases are transmitted through (1) water (drinking, bathing, washing utensils, vegetables, fruits, etc.); (2) foodstuffs (sausages, fish, etc.) in which the microbes develop to increase their toxicity; (3) by direct or indirect contacts (through cloths, utensils, books, etc.) of healthy people with infected persons; (4) through inhaled air; (5) by insects (lice, flies, mosquitos, ticks, etc.).

The spreading of the epidemic depends on the susceptibility of the population and the animals in the given area to this particular infection. The living conditions of people, their neatness and tidiness, prophylactic measures, and timely revealing of the carriers limit the spreading of the disease.

As a rule, sources of water get contaminated with pathogenic microbes by sewage. It get into water by accidental spills and breakdowns in the sewage system or nearby sewage treatment plants.

Rivers and lakes get infected with pathogenic microbes when sewage is discharged directly into open water bodies or get into them with runoffs.

Well water can be infected by surface runoff in ample rainfalls.

The epidemic spread can be controlled by purification and disinfection of water.

Personal hygiene (especially cleanliness of the hands), the sanitary state of dwellings, yards and the environment, are very important in the eradication of epidemics. The human body has certain properties which protect him from occasional ingress of pathogenic microbes. For example, the skin is not only the mechanical obstacle to microbes, but it excretes some substances that kill microbes precipitated on it. Typhoid bacilli and other pathogenic bacteria very soon perish on the skin of well washed hands. The mucosa of the mouth, nose, eyes, the upper respiratory ways and other organs secrete substances which kill microbes. The human saliva also has bactericidal properties. Some microbes are killed by gastric or intestinal juice and bile.

But the natural protective mechanisms are often insufficient to rebuff the attack of pathogenic microbes. Toxins of many microbes cause necrosis of cells on the attacked site of the mucosa, after which the microbes invade the living body to cause its infection.

If a given organism is immune toward a particular causative agent, the disease does not develop. An immune body has special means by which the microbial toxins are neutralized or the microbes themselves are killed. Disinfection of excrements of an infected man, of his belongings and the room, and rodent control are very important means to stop the infection spreading. An effective method of fighting the causative agents of the infection in water is the proper work of the water treatment plants.

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## 11.18. Indicating Role of *Escherichia Coli*

The degree of water pollution with pathogenic bacteria is determined by the presence in it of *E. coli*, which are found in the intestine of man and animals. These bacteria are harmless to man but their presence in water indicates that it is polluted with human and animal excrements and there exists a danger of presence of causative agents of dysentery, typhoid fever, cholera and other grave diseases.

It is difficult to isolate pathogenic bacteria in water during its bacteriological analysis, and the bacteria of the *E. coli* group are therefore determined since their quantity is indicative of the pollution degree. The content of *Escherichia coli* in open water bodies varies with seasons. Their level sharply increases after heavy rainfalls and in spates. The following degrees of water pollution are distinguished depending on the content of *E. coli* in water: heavily polluted (over 10,000 bacteria in one litre), polluted (1000 bacteria), slightly polluted (100 bacteria), satisfactory quality (10 bacteria in one litre), drinking water (3 and less bacteria in one litre).

The degree of pollution is designated by coli-titer and coli-index. *Coli-titer* is the smallest volume of water, in millilitres, containing one *E. coli*. *Coli-index* is the number of *E. coli* contained in 1000 ml of water. According to the Soviet State Standard (ГОСТ), the coli-index of drinking water should not exceed 3, and the coli-titer, not less than 300.

Faecal pollution of water is established by the presence in it of *E. coli* group bacteria with bacteria of the subgroups, *Bacterium paracoli* and *Bacterium aerogenes*. The organisms indicating the faecal pollution of water are characterized by the following signs: these are aerobes, weakly motile, gram-negative, nonsporulating bacilli which do not thin gelatin, form indole, coagulate milk, and ferment glucose, lactose, maltose, levulose, arabinose, and mannitol, with formation of gases ( $H_2$  and  $CO_2$ ). They do not ferment saccharose. When cultivated on Endo's medium, these bacteria form red, with golden luster, dark red, and pink with dark centre colonies.

At the present time, all variants of *E. coli* capable of reacting with acids and liquid media containing glucose or mannitol, with liberation of gases at a temperature of 43°C during 18-24 hours, are considered to be indicators of recent pollution of water with faecal effluents. It should be emphasized that *E. paracoli* are usually found in people with intestinal infections, and special attention should be given to treatment of water containing these microbes.

*Streptococcus faecalis* (a variety of the greening streptococcus group bacteria) are used as indicator-microbes in some foreign countries. Enterococci comprise a group of microorganisms with easily distinguishable specific signs. According to Kalina (1974), a comparative analysis of the indicator role of *E. coli* and *Str. faecalis* in various effluents reveals a clear dependence of the enterococcus index on occurrence of pathogenic enterobacteria. These relationships were absent during comparison of occurrence of pathogenic enterobacteria and the *E. coli* group bacteria.

Similarity of behaviour of enterococci and pathogenic enterobacteria in sewage emphasizes the advantage of enterococci as indicator-microbes.

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## 11.19. Microbes in Nature

**Microflora of Air.** Air is not a suitable medium for the growth of microorganisms. It contains little moisture, nourishment is poor, and the organisms are exposed to direct sun radiation. Microbes get into air with dust or with droplets of liquid (e.g. during sneezing). Settling dust precipitates microbes.

Microflora of air is meagre and occasional. It depends on the microflora of the soil in a given area.

Greater amounts of microbes are contained in the dust-laden air over towns and cities.

The air becomes more clean with elevation from the ground. Each litre of air at an altitude of 500 m over Moscow contains not more than three bacteria, at 1000 m, 1.5, and at an altitude of 2000 m, only 0.5 bacteria in one litre. The least number of bacteria is contained in air in winter, and the maximum in summer. In winter, the soil is isolated from the air by snow, while in summer microbes, together with soil, are carried by the wind and lifted into the air.

The air of enclosures is richer in bacteria in winter because man stays in an enclosure for longer time in the cold season.

**Microflora of Soil.** Soil is the most suitable medium for the development of microorganisms. It protects them from direct sun radiation, nourishment is ample, and moisture is present in sufficient quantity. All soils of the globe are therefore inhabited by microbes. But the density of their populations is different in various areas. One gram of soil can contain from dozens of microbes to hundreds of millions, depending on the area from which the soil samples are taken.

The density of microbial population depends on the temperature, physico-chemical composition of soil, and its moisture content.

The greatest microbial populations are found in the upper layers of the ground. The number of microbes decreases with increasing depth, and they are in scant quantities on the surface because direct sun radiation kills microbes.

By the type of nourishment, all microbes inhabiting soils are divided into autotrophic and heterotrophic.

Microbes actively change the composition of the soil and at the same time they change themselves. The quantitative factor of these changes can be illustrated by the fact that only one group of soil-dwelling bacteria (liberating carbon dioxide by decomposing organic matter) can liberate into the atmosphere about 7500 cu.m of  $\text{CO}_2$  from the surface area of one hectare during a year.

**Microflora of Water.** Water of open bodies contains sufficient nutrition to maintain the development of microorganisms. The richer in organic matter, the greater quantity of microbes can water contain. The water in a river always becomes richer in bacteria after it passes a town.

There is a certain regularity in distribution of bacteria in standing water bodies (ponds, lakes). The water assess adjacent to the banks are always richer in microorganisms than in deeper parts. The greatest amounts of microbes are contained at depths from 5 to 20 metres.

The studies have shown that there is no direct dependence of the number of bacteria on the concentration of nutrients in deep layers of water. It shows that the store of nutrients in water greatly exceeds the requirements of the microflora

The greatest populations of microorganisms are found in water from May to July, although the nutrient content of water is not the maximum during this period. It is probably explained by the temperature changes in water. The number of bacteria in water sharply increases after rainfalls, and decreases in bright weather. Bottom sludge is always richer in bacteria than water itself. The superficial layer of the bottom deposits is the richest in bacteria. A kind of bacterial film is formed on the superficial layer of the sludge, and its function in the life of a water body is evidently quite significant. Filamentous sulphur bacteria and iron bacteria are especially important. Sulphur bacteria oxidize hydrogen sulphide to sulphates to protect fish. When the bottom film is destroyed by heavy storms, fish is poisoned in great quantities.

Fermentation processes occur at the bottom of water bodies. The processes liberate  $\text{CH}_4$  and  $\text{CO}_2$ .

Each gram of sludge contains about (a) 100,000 to 1,000,000 bacteria reducing sulphates; (b) from 10,000 to 100,000 thione bacteria; (c) about 1000 nitrifying bacteria; (d) from 10,000 to 100,000 denitrifying bacteria; (e) about 100 anaerobic and 100 aerobic destroyers of cellulose.

The bottom sludge contains also bacteria oxidizing methane and hydrogen, inducers of fermentation, anaerobic fixers of atmospheric nitrogen, etc.

Water contains mainly nonsporeforming bacteria (about 97 per cent) while the sludge contains mainly sporeforming ones (about 75 per cent). The deeper the sludge, the greater amounts of spore-forming bacteria it contains.

Bacteria are abundant in the water of seas and oceans. One millilitre of water taken from shallow lakes contains about 250,000 bacteria. If the water is 10 meter deep, the mass of bacteria collected from an area of one square kilometer would be as large as one ton. And only to think, that one billion bacteria weight only 0.5—0.7 milligram!

The microbial population of water is an important factor of mineralization of organic matter in a water body. Moreover, it is an important link in the trophic chain of fishes.

Sea bottom sludge is especially rich in microbes: one gram of sludge, according to Butkevich, contains  $367.4 \times 10^6$  bacteria, which weigh only 0.3 mg.

Bacteria can be found in the remotest parts of the North Ocean. B. L. Isachenko found nitrifying, denitrifying bacteria, and also bacteria reducing sulphates and assimilating atmospheric nitrogen (*Azotobacter* and *Cl. pasteurianum*) at depths to 100 m, the total depth of the sea being 180 m. Marine microbes best develop in water containing 2-3 per cent of sodium chloride.

Subsoil waters (artesian, spring water) contain about ten bacteria

in one millilitre. This low bacterial content can be explained by their adsorption on soil particles as water passes the ground.

Rain water and fresh snow are also poor in bacteria (not more than 10 bacteria in 1 ml), especially so if the air is not polluted with dust. Precipitation over a dusty town contains to several hundreds of bacteria in 1 ml.

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## 11.20. Ecological Classification of Waters

Ecology is the science of mutual relationships between organisms (animal or plant) and the environment.

Any water body has complicated biological communities of microorganisms. Each degree of water pollution with organic substances corresponds to definite microflora and microfauna. Hence a possibility arises to establish the degree of pollution by the presence of indicator-organisms in a given water body. The presence of such organisms indicates the quality of water; or the quantity of microorganisms in a water body can be used to establish the degree of its pollution.

1. *The heaviest pollution (polysaprobic)*. Putrefactive anaerobic processes occur in the zone of polysaprobic pollution, since water here is rich in remnants of dead plants and animals, i.e. proteins, fats, cellulose, and the products of their decomposition. Organisms resistant to increased doses of organic matter, hydrogen sulphide, carbon dioxide and methane develop in this zone. The number of bacteria is to 1,000,000 in one millilitre.

2. *Medium pollution (mesosaprobic)*. Organic matter is mineralized in this zone, the oxidizing processes prevailing. The nitrogen of ammonium salts is converted by microbes to nitrites, hydrogen sulphide into sulphates. Organic matter is mineralized to  $\text{CO}_2$ .

Mesosaprobic zone is divided into alpha- and beta-mesosaprobic zones. They differ by the intensity of oxidation processes. The most intense mineralization occurs in the beta-mesosaprobic zone, where organic matter is fully mineralized. The number of bacteria here is from 100,000 to 1,000,000 in one millilitre.

3. *Pure water zone (oligosaprobic)*. Organic matter is absent. The processes of oxidation of nitrites to nitrates are completed here. The microbial content of water is from 1000 to 10,000 in one millilitre.

Typical representatives of this zone are iron bacteria which oxidize ferrous iron into the tervalent metal.

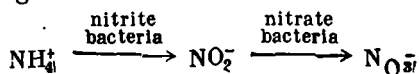
## 11.21. Biological Factors of Water Self-Purification

Microflora and microfauna, which occur in water bodies due to their pollution with organic matter, take an active part in the process of self-purification. The kingdom of organisms is quite varied. This variety depends on the ecological factors, e.g. physical properties of water (density, viscosity, refractive index, presence of organogens, etc.), the illumination conditions, oxygen supply, temperature, and the movement of the water masses.

As has been said above, these factors are completed with biological characteristics of microorganisms, namely, their adaptability to the environment. Various microorganisms differently react towards light, temperature, oxygen, nitrogen, carbon, sulphur, calcium, silicon, and organic substances. Their dependence on various factors is different.

Relationships between the organisms inhabiting one and the same medium can be symbiotic or antagonistic. The former case is known as *metabiosis* (the dependence of one organism upon another for its existence), while the latter is called *antibiosis* (the condition when an association between antagonistic organisms is detrimental to one or both of them).

An example of metabiosis is *nitrification*, i.e. the process of oxidation of the nitrogen of ammonium salts into nitrites and nitrates



The oxidation is effected in two phases, by two types of bacteria. Nitrite bacteria oxidize the nitrogen of ammonium salts to nitrites which are accumulated in the medium and are the starting material for the development of nitrate bacteria.

A partnership of different organisms based on the mutual benefit, where dissimilar organisms provide a favourable medium for the development of each other is called *symbiosis*. An example of symbiosis is the association of the nodule bacteria with leguminous plants. Nodule bacteria take nitrogen-free organic compounds and mineral salts from the leguminous plants and give them back the nitrogen-containing compounds which they synthesize from atmospheric nitrogen.

Symbiotic relationships occur also between some forms of lactic acid bacteria, yeast, and putrefactive bacteria (used in the production of kefir).

In antibiosis, on the contrary, antagonistic relationships arise between dissimilar organisms, and the products yielded by one organism can be detrimental to another.

The mechanism of antagonistic action in microorganisms can be different. In some cases, they compete for nourishment, in others the antagonistic microbes form much acid to provide the conditions in which other types of microorganisms cannot live.

Antagonistic microbes often liberate specific chemical compounds as their metabolites. When these are accumulated in the surrounding medium, they inhibit the growth and propagation of other microorganisms, and sometimes completely destroy them. Some chemical compounds produced by microscopic fungi and bacteria are called *antibiotics*.

The antagonism of microbes is important in medicine and in industry.

Antagonism of bacteria is employed in methane tanks, special plants intended for digestion of sewage sludge. The growth of methane bacteria is restricted by butyric acid bacteria which liberate volatile fatty acids. The process is therefore controlled so that the growth of butyric acid bacteria should be inhibited.

A community of microorganisms, which is beneficial to one and detrimental to the other organism is called *parasitism*. An example of this kind of symbiosis is occurrence of tuberculosis bacilli in animal tissues, helminth eggs in the intestine of man and animal. Viruses parasitizing on living cells of animal and plant tissues is another example.

The symbiosis of organisms is often based on the difference of their functions. For example, the bacteria decomposing proteins with liberation of hydrogen sulphide provide favourable conditions for the development of sulphur bacteria (metabiosis). Associations of microorganisms, called biocenosis, are thus formed.

Two types of biocenosis are distinguished: benthos and plankton.

Plankton is a collective name for the minute free-floating organisms, of both animal and plant origin.

Benthos is the flora and fauna of the oceanic bottom, and subwater objects. These microorganisms grow on subwater parts of ships, harbour structures, and other objects.

Microorganisms differ from one another depending on the ecological factors: marine organisms, fresh-water organisms, organisms inhabiting salt-water lakes, swamps, rivers, springs, pools, waterfalls, hot springs, and sources of mineral water.

The microorganisms inhabiting a given water body take an active part in the purification of water. They mineralise organic compounds and oxidize reduced substances of inorganic origin (e.g. divalent iron into trivalent iron, ammonium to nitrites and nitrates, hydrogen sulphide to sulphates, etc.). Hence organic substances polluting water provide the conditions for the development of microorganisms which mineralize them to purify the polluted water.

The self-purification is also facilitated by the antagonism of microorganisms in a water body, the action of direct sun radiation, and dilution of the water with pure water from nonpolluted sources.

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## 11.22. Technical Means of Controlling Microbial Population of Water

Polluted water contains various organic substances at various stages of their mineralization. When microorganisms are used to destroy these substances, conditions favourable for the growth of the required complex of organisms are created. By acting on the biochemical process in the desired direction, the specific biological properties of these organisms can be utilized.

From the practical standpoint, all microorganisms are divided into useful and harmful.

*Useful* microorganisms are many saprophytes and their companions, which destroy organic substances to carbon dioxide and water in aerobic conditions and to simpler organic compounds, such as alcohols, volatile fatty acids, methane, and carbon dioxide, in anaerobic conditions.

*Harmful* microorganisms are pathogenic microbes. When contained in excess quantities, useful microbes produce a harmful effect on water purification and can be called harmful as well.

Technical means of controlling the growth of useful microbes and the biological processes induced by them are as follows:

*Temperature Control.* It has been established that if temperature is raised 10°C, the velocity of the biological process increases 2-3 times. The decreasing temperature produces the reverse effect. The sludge in methane tanks is heated artificially to 35-55°C.

*Oxygen Supply.* The intensity of the process in aeration tanks is controlled by dosing air (oxygen) delivered into them. And on the contrary, oxygen is held back from the apparatus where anaerobic processes occur (in septic tanks, methane tanks, two-level settling tanks).

*Nourishment Supply.* All microorganisms consume substances containing organogens (C, H, N, P, S). Whenever either of these elements is absent in water, it should be added artificially. Domestic (municipal) sewage is rich in these elements and it is therefore often added to e.g. effluents of the dyeing-bleaching plants.

*Optimum pH of the Medium.* Many microorganisms are very sensitive toward the hydrogen ion concentration. Therefore, when the medium reacts acid, it is neutralized by adding alkaline effluents or is alkalyzed by lime.

*Removal of Noxious Substances.* The content of poisons or disinfectants should be decreased to concentrations harmless to microorganisms. Water containing arsenic, mercury, copper, acid or alkali, should not be admitted to the treatment plants. Chlorides of Hg, Pb, Cu, Fe, and Zn are especially dangerous.

It has been established that corrosive sublimate, when contained in concentrations to 0.000005 per cent, stimulates the growth of microbes, while the concentration of 0.007 per cent kills them immediately.

Many causative agents of infectious diseases are transmitted to man and animal through the agency of water. It can contain causative agents of typhoid fever, paratyphoid A and B, dysentery, cholera, infectious jaundice, plague, helminth eggs, etc.

These microorganisms can for a long time stay in water but when they get into a living body they adapt themselves to the new conditions and cause the corresponding disease.

Special water-storage basins and lakes are made artificially for water supply purposes. Fauna and flora populate the entire thickness of the water layer. By the time when the nourishment available in a given water basin is exhausted the microflora is partly destroyed by the fauna as well; and bacteriophages complete the destruction of harmful bacteria.

Modern epidemiology widely uses sanitary-engineering methods of fighting infectious diseases by disinfecting water. The methods comprise chemical and physical sterilization and disinfection; they also provide unfavourable conditions for the growth of pathogenic microbes.

## CHAPTER TWELVE

# LIFE OF MICROORGANISMS IN WATER-SUPPLY SYSTEMS AND SEWAGE TREATMENT PLANTS

When drinking water is settled and percolated, microorganisms are retained on the surface of fine-pore material and take part in the formation of deposits in water pipes.

It has long been noticed that the number of bacteria decreases significantly in the process of settling. Strange as it may seem at first sight, the microorganisms are killed the sooner, the heavier the pollution of water. The paradox is explained by the antagonistic action of microorganisms. The number of bacteria decreases during the first two days of settling, and then algae propagate in settling tanks. When algae die, they are destroyed by putrefactive bacteria. The organoleptic properties of water are deteriorated, the dissolved oxygen content is depleted, and the oxidation potential drops.

Microbiological processes occur in settling tanks and receptacles of water. These are connected with the decomposition of organic substances in anaerobic conditions.

*Phytobenthos* often develops on the sludge surfaces in settling tanks. Biocenosis of benthos consists of blue-green algae. When they propagate, they give unpleasant odour to the adjacent layers of water.

When natural water is passed through slow filters, a biological film is formed on the surface of the filtering sand. The biocenosis of the film is represented by microorganisms (nitrifying bacteria, sulphur bacteria) and benthos forms (zoo- and phytobenthos, i.e. animal and plant communities). The depth of life in this film normally does not exceed a few centimetres.

Microflora develops even on fast filters in warm seasons. The amounts of nitrogen of ammonium salts decreases and of nitrites and nitrates increases in summer.

**Microbiological Growths in Pipes of Sewage Treatment Plants.** Microorganisms grow inside water pipes to decrease their inner diameter; they destroy rubber, wood, and other materials.

Bacteria and algae take part in this growth. What is common in all these organisms is that they are all aerobes.

Filamentous sulphur bacteria oxidize  $H_2S$  to  $S$ . These bacteria grow in patches of grey hair. When they enter water pipes they clog them.

Some actinomycetes (the microorganisms forming very fine mycelium) and molds live on rubber and use the carbon of natural or artificial rubber to synthesize their own bodies. Therefore they rapidly destroy rubber.

Pipes are clogged mechanically by iron bacteria, molluscs, and some algae (Figs. 12.1 and 12.2). Molluscs precipitate  $CaCO_3$  from water. Water pipes become overgrown with microbes which die to give unpleasant odour and taste to the water.

The following measures should be taken to prevent this overgrowth:

1. Protection of water bodies and streams from domestic and industrial sewage.
2. Removal from water of  $H_2S$ ,  $Ca^{2+}$ ,  $Fe^{2+}$  and other elements which promote the growth of microorganisms responsible for the overgrowths.
3. Mechanical cleaning of the bottom and banks of water bodies from aquatic plants.

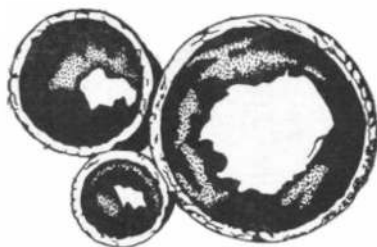


Fig. 12.1. Water pipes overgrown with iron bacteria

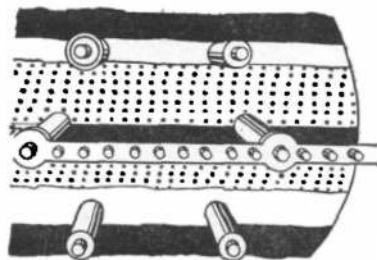


Fig. 12.2. Condenser of a steam turbine overgrown with bacteria

## CHAPTER THIRTEEN

# TREATMENT OF SEWAGE WITH MICROORGANISMS

The sewage treatment consists in the separation of solid and liquid phases and their further treatment in aerobic and anaerobic conditions. The aerobic treatment gives activated sludge and active film, while anaerobic treatment gives septic or digested sludge. In both cases the rate of mineralization depends on the mass (to be more exact, on the surface area) of the microbes involved, and on their contact with the pollutants.

Anaerobic and aerobic treatments consist of the following processes:

(1) adsorption of pollutants on activated sludge, biological film, or septic sludge, etc.

(2) mineralization of pollutants with microorganisms.

The former process occurs rapidly (during 10-15 minutes) while the latter takes considerable time. The time of desorption depends on the conditions of the plant operation, temperature intensity of mixing fresh material with the mineralizing agents, on the oxygen supply, and on many other factors.

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### 13.1. Aerobic Treatment of Sewage

The liquid phase of the sewage is treated in aerobic conditions. The process takes place in (a) aeration tanks, (b) biological filters, (c) biological ponds, (d) irrigation fields and filtration fields (land treatment). Sewage treatment plants differ in their design, but they all are intended to use aerobic oxidation by atmospheric oxygen in the active substrate.

**Biological Filters.** These use slags, gravel and other materials which are sprayed over with sewage after treatment in primary settling tank.

Biological filters are of different design and capacity (per square metre of the packing). They are classified as trickling, high-capacity, tower, and plastic filters.

In *trickling filters*, their surface is sprayed over uniformly at short intervals, sewage being delivered in drops or jets. Air is delivered to the filter by natural ventilation through the open surface of the filter and through the drains.

Trickling filters are packed with comparatively small particles, measuring from 25 to 30 mm. Their capacity is not high and normally varies from 0.5 to 1 cu.m. of sewage per cubic metre of the filter per day. The cleaning effect is high. The total BOD of the sewage delivered onto the filter should not exceed 220 mg/litre. If a trickling filter is used for complete purification of water, its total BOD should not exceed 15 mg/litre.

Trickling filters require careful handling and maintenance. If the filter is overloaded with organic substances, the filtering surface soon becomes clogged and efficiency of the filter is quickly decreased.

*High-capacity biological filters* differ from trickling filters by their high oxidizing power, which is attained by its special design. The grains of the packing are larger than in trickling filters (from 40 to 65 mm). This increases the permissible load on the filter. The special design of the bottom and drains ensures artificial aeration of the unit. The comparatively high rate of sewage passage through the filter ensures constant removal of difficultly oxidizing insoluble substances and the exhausted biological film from the filter.

When concentrated sewage is treated, it is diluted with treated sewage containing microorganisms adapted to the given pollution which intensifies mineralization of organic material. High-capacity biological filters treat sewage to any desired degree of purity and are therefore used for partial and complete purification of sewage.

During the commissioning period, a biological film is formed on the lumps of the packing. The main agent of the biological film is its microbial population which oxidizes organic substances.

*Biocenosis of the biological film* in biofilters comprises algae (blue-green, green, diatoms), protozoa, insect larvae, small beetles, worms, fungi, and bacteria. Green and blue-green algae grow in the upper layers of the filter (from 0 to 10 cm, Fig. 13.1), but slightly below the sprayed zone where sufficient quantity of oxygen and light, necessary for their growth, are available. Diatomaceous algae live in deeper layers since they need no light or much oxygen. But they cannot grow in full absence of oxygen. The diatoms are more frequently found in the lower parts of the biological filters than at bottom (from 10 to 50 cm). This holds for both sprayed and non-sprayed parts of the packing.

The habitat of protozoa is the nonsprayed zone of the upper layer and both sprayed and nonsprayed zones of the bottom layer.

The zone of worms are the lower layers of the biological filter (sprayed parts).

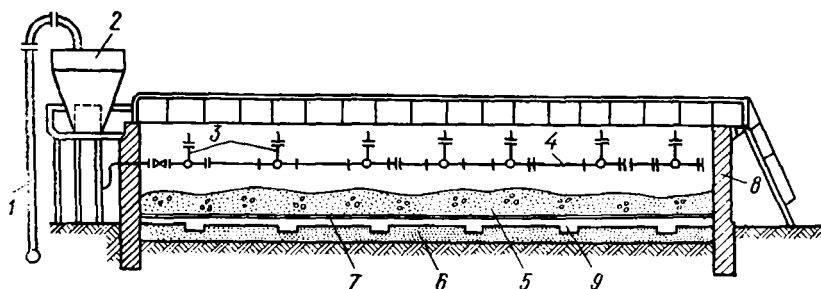


Fig. 13.1. Biological filter:

1—inlet pipe; 2—batcher; 3—sprinklers; 4—distribution network; 5—filter packing; 6—solid bottom; 7—perforated bottom (drains); 8—walls; 9—troughs in solid bottom

Bacteria live in the entire mass of the biological film. They are represented by alpha- and beta-mesosaprobic groups.

Mean quantities of the above named organisms, per cubic metre of slag of the inhabited zone, are as follows:

Green algae	$226 \times 10^9$ cells
Blue-green algae	$143 \times 10^9$ cells
Diatoms	$24 \times 10^9$ cells
Protozoa	$66 \times 10^9$
Worms	$181 \times 10^4$
Insects	$9 \times 10^9$

All representatives of the animal and plant kingdoms take an active part in the treatment of sewage. Bacteria mineralize organic materials, protozoa (infusoria and rhizopods) feed on bacteria, while algae produce oxygen and phytoncides (substances detrimental to microorganisms). Worms dig passages between slag particles to loosen the biological film and to ensure the oxygen access to it. Moreover, the worms feed on organic substances to digest and destroy some stable compounds such as chitin and cellulose.

The biocenosis of the active film is very sensitive to the temperature changes. The process is much slowed down at low temperatures.

The relative quantity of sludge in biological filters is 25-50 times greater than in aeration tanks. The amount of activated sludge in aeration tanks (as dry substance) is only 2-5 grams per litre, while in biological filters it is about 100 g per litre. The oxidation rate should therefore be greater on biological filters than on aeration tanks. The purification process in aeration tanks ends in 4-10 hours, while on biological filters it continues only for 1-2 hours.

The efficiency of biological filters is assessed by the oxidizing power of a unit, which is measured in grams of pollutants (determined by the total BOD) mineralized by the active film on a square meter of the packing (g/cu.m).

The relative capacity of a biological filter varies within a wide range since it depends on the temperature of the sewage, the ambient temperature, the composition of the sewage, the material of the packing, the method by which air is delivered, the type of the unit, etc.

The load on a biological filter is determined by the amount of water delivered per square metre of the packing per day or by the total BOD per cubic metre of the packing material per day. The permissible deviations in the load on biological filters of various design, as calculated for the full biological purification of sewage, are given in Table 13.1.

Table 13.1  
Loads on Biological Filters

Biological filter	Packing height, m	Load	
		water, cu.m/sq.m per day	total BOD, g/cu.m per day
Trickling filter	2	1-3	100-300
High-capacity filter	4	10-30	500-1500
Tower filter	8	30-50	800-1400
Plastic packing filter	4	30-45	1600-2200

But even the best aeration filters fail to ensure complete purification of water. The treated liquid contains organic substances and microorganisms. It is therefore treated with free chlorine or chlorine-containing compounds after the treatment on aeration filters. The dose of active chlorine is determined experimentally.

**Aeration tanks** (Fig. 13.2). These are reinforced concrete rectangular reservoirs. They consist of sections divided lengthwise by partitions, which do not reach one end of the tank, into 2, 3 and 4 passages. The capacity of the unit is determined by the amount of sewage it can hold and by the degree of sewage pollution (total BOD). The working procedure consists in slowly passing sewage mixed with activated sludge through the tank. Air is delivered into the tank by blowers (compressors, fans); it is also trapped mechanically from the atmosphere through porous plates on the tank bottom and mixed with the liquid by stirring or by creating shallow turbulent currents.

The atmospheric oxygen provides conditions for the life of saprophytic microorganisms to partly inhibit the growth of pathogenic microorganisms. Aeration promotes also a more effective contact of activated sludge with the sewage.

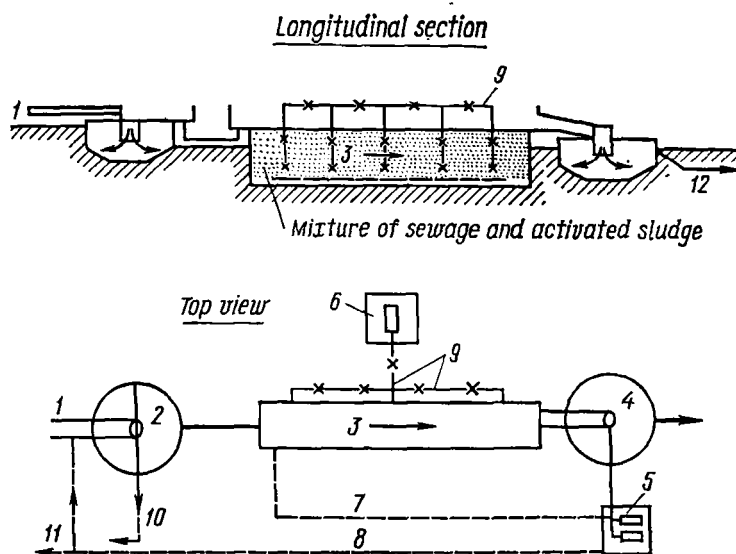


Fig. 13.2. Aeration tank for complete purification of sewage:

1—inlet pipe; 2—primary settling tank; 3—aeration tank; 4—secondary settling tank; 5—activated sludge pumps; 6—air blowers; 7—return activated sludge; 8—excess activated sludge; 9—air ducts; 10—fresh sludge; 11—excess activated sludge in compacting section; 12—treated sewage

The work of aeration tanks is characterized by the formation of bacterial flocs with activated sludge which are capable of rapid sedimentation and separation from the treated liquid. Some authors explain the formation of these flocs by the change of the surface charge of the bacterial cell. This process can be compared with coagulation of finely dispersed suspensions.

**Biocenosis of Activated Sludge.** Activated sludge is formed in aeration tanks from suspended particles contained in sewage, by adsorption of colloids, and multiplication of microorganisms on this substrate.

The activated sludge comprises the whole complex of microbes contained in sewage, including the pathogenic flora of man. The microbes are adsorbed on activated sludge and, depending on their physiological properties, become adapted to the surrounding medium to enter the complex of mineralizing agents. Part of flora which cannot adapt to new environmental conditions is killed and the mineralizing microbes feed upon it.

The main component of activated sludge are bacteria. One gram of activated sludge contain  $1 \times 10^{12}$  bacteria, whose overall surface area is 1200 square metres. The bacteria are alpha- and beta-mesoprobic groups. Their composition (with respect to species) depends

on the composition of the pollutants. The biocenosis of activated sludge develops in pronounced aerobic oxidizing conditions. Therefore, along with other microbes, the sludge contains nitrifying bacteria (to  $3 \times 10^7$  per gram of activated sludge). In addition to unicellular bacteria, small amounts of filamentous bacteria, yeast, and separate hyphae of molds also develop in activated sludge. Microfauna of activated sludge is represented mainly by one-cell animals, protozoa, but more complicated representatives of the animal kingdom, e.g. rotifers and roundworms, also live in activated sludge. Among unicellular animals there are sarcoids, flagellates, ciliated and sucking infusoria.

The entire population of activated sludge takes part in mineralization of organic substances.

If an aeration tank works properly, an equilibrium is established between all representatives of microflora and microfauna. The upsetting of this equilibrium is regarded as a signal indicating the deterioration of the work of the treatment plant, since the change in the quantitative composition of the microbial population in activated sludge is preceded by a marked change in the physicochemical properties of the treated liquid.

The most favourable condition for the treatment of sewage in aeration tank is at the ratio of the total BOD : N : P = 100 : 5 : 1.\* If these elements are in deficient quantities, they should be added to the system. Nitrogen should be added as ammonium salts, and phosphorus as superphosphate or trisodium phosphate.

When settled sewage is delivered into an aeration tank it is mixed with activated sludge. Its dose in grams of dry substance per litre of settled sewage depends on the total BOD and on the design of the aeration tank. For example, 3.4-3.7 g/litre of sludge is required for an aeration tank provided with a secondary settler for regeneration of activated sludge if total BOD is to 150 mg/litre, and 4-5 g/litre if total BOD is to 200 and over. The dose is approximately halved for aeration tanks working without regenerators.

The quality of activated sludge is characterized by the *sludge index*, which is a volume, in ml, occupied by damp sludge after a 30-minute settling with one gram of dry substance. When the sludge index is determined, a sample of sewage is shaken thoroughly with moist sludge, transferred into a 100-ml measuring cylinder and allowed to stand for 30 minutes. The volume occupied by the sludge is measured in millilitres and the dry substance of activated sludge, in grams. The sludge index =  $v/g$  ml/g, where  $v$  is the volume of sludge in ml, and  $g$  is the dry weight of the sludge, in grams.

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\* SNiP (Construction Norms and Regulations), 11-32-74, Part II, Ch. 32, Moscow, 1975 (in Russian).

Dense, well precipitating sludge has the index of about 60 ml/g, a looser sludge has the index of 80-90 ml/g, and the sludge index over 300 ml/g indicates inadequate work of the treatment plant.

The velocity of precipitation of activated sludge flocs depends on its density, which, in turn, depends on the composition of microflora. Minute microorganisms form a dense, quickly precipitating activated sludge, while long filamentous and branched organisms precipitate in a loose difficultly precipitating sludge.

The causes of faulty operation of aeration tanks are overloading with organic substances, the formation of anaerobic zones, deficient quantities of biogenic elements, sharp fluctuations of temperature or pH of the medium, ingress of toxic substances into the treated sewage, etc.

According to N. A. Bazyakina, activated sludge has the following chemical composition (in per cent, as dry substance at 100°C): ash, 15.58; silica, 3.95; iron oxide, 1.58; phosphoric anhydride ( $P_2O_5$ ), 2.14; organic nitrogen, 3.61; crude fat, 2.51; and fatty acids, 0.39.

**Operation of an Aeration Tank.** Complete and partial biological treatment can be given to sewage in aeration tanks. Biological treatment is complete if the biochemical processes proceed to the beginning of the nitrification process (biochemical oxidation of nitrogen of ammonium salts to nitrites and nitrates). Incomplete biological treatment consists only in partial mineralization of organic materials to 40-80 per cent of the total BOD.

The degree of purification is determined conventionally by the residual BOD of treated sewage. The total BOD of sewage after complete biological treatment should be less than 20 mg/litre, and after partial purification, greater than 20 mg/litre.

After standing in the primary settling tank, the sewage is delivered into an aeration tank and mixed with activated sludge. The mixture is intensely aerated along the entire length of the tank (Fig. 13.2). This is necessary to supply sufficient air and to maintain the sludge in the suspended state. The mixture is then transferred to the secondary settling tank where the sludge is separated from the treated sewage. The clarified liquid is transferred onto a disinfecting unit and then discharged into a water basin. After regeneration in the secondary settling tank, the sludge is reused in the aeration tank where it is mixed again with new portion of sewage.

Activated sludge has a tremendous adsorbing power due to a well developed surface area. The adsorbing surface activated sludge gradually diminishes with time and is recovered by the microorganisms inhabiting activated sludge. The process is known as regeneration of sludge. It is effected in the aeration tank, in the secondary settling tank, or in special reservoirs, regenerators, in conditions of strict aerobiosis. But the bulk of the biomass increases as the pollutants are oxidized, and excess sludge is removed from the secondary

settling tank to be treated together with the sludge of the primary settling tank.

The following changes occur in the liquid treated in aeration tanks: (1) the concentration of pollutants decreases due to dilution with the liquid carrying activated sludge; (2) pollutants are adsorbed on activated sludge during the first 15-30 minutes (the first oxidation stage); (3) the amount of organic material dissolved in water and adsorbed on activated sludge gradually decreases (the second stage of oxidation); (4) the nitrogen of ammonium salts and nitrites gradually diminish due to their oxidation to nitrates (the third oxidation stage); the process is called nitrification (Fig. 13.3).

The second and the third oxidation stages continue for a few hours. The work of the treatment plant is successful on the condition that the pH of the medium falls within the range of 6.8-8.5, and the concentration of noxious substances in water does not exceed the specified maximum.

Aeration tanks can be run the whole year round, since organic substances continue their conversion into mineral substances at low temperatures as well. But nitrification is slowed down in the cold season.

The number of bacteria in water treated in the aeration tank is sharply decreased. For example, *E. coli* bacteria are removed to 98 per cent of their initial quantity.

The number of bacteria is reduced by adsorption on activated sludge, by their destruction by the fauna, and by the dissolution in bacteriophages.

But the aeration tank cannot ensure complete purification of water from pathogenic microorganisms, and before discharging into a water body, the treated water should be disinfected.

**Control of an Aeration Tank Operation.** If the procedure in an aeration tank is violated, the density of sedimented flocs decreases and they float to the surface from the depth of the liquid. The mixture of the sewage and sludge becomes turbid. Many investigators have come to a conclusion that the density of activated sludge decreases due to an intense development of filamentous bacteria (to 5000  $\mu$  long) which determine the structure of the sludge flocs. According to some authors such a burst in the development of filamentous is

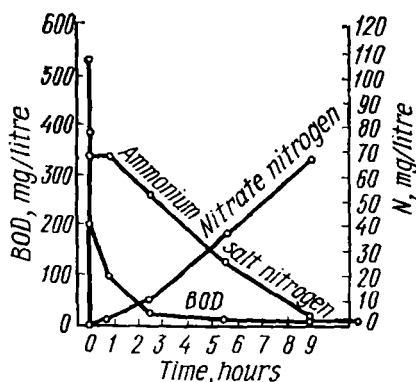


Fig. 13.3. Changes in the chemical composition of sewage in an aeration tank

due to the disordered balance between the concentrations of activated sludge, nutrients, and oxygen. The disbalance inhibits the development of saprophytic microflora (zooglea) to provide favourable conditions for the growth of filamentous bacteria.

The growth of filamentous bacteria is controlled by alkalyzing the medium to pH 9-9.4 or by acidifying to pH 5.

*The Role and Importance of Some Groups of Organisms in the Mechanism of Biological Treatment of Sewage.* The main mineralizers of organic matter are bacteria. Sarcoids feed on sludge to convert complicated substances into simpler ones which can be consumed by other organisms. Infusoria and other protozoa are, according to some authors, regulators of bacteria growth who provide favourable conditions for the mineralization to promote flocculation of finely dispersed suspensions by the liberation of mucilage into the surrounding medium. Protozoa promote accumulation of nitrogen in the surrounding medium to add to the valuable qualities of activated sludge as a fertilizer. Moreover, protozoa and rotifers perform the role of indicators\* which characterize the work of the sewage treating plant. Table 13.2 shows the relationships between the growth of these organisms and the intensity of operation of the plant.

Table 13.2

Development of Various Protozoa and Rotifers  
Depending on the Intensity of Work of Sewer Treatment Plant

Characteristics of work of biological oxidizer	Organisms			
	ameba (limax)	colourless flagellates	infusoria	rotifers
Bad	prevail		absent	
Unsatisfactory	prevail		meagre	
Satisfactory (weak nitrification)	single species		holotricha prevail	prevail
Good (intense nitrifica- tion)	absent		peritricha and gastrotricha prevail	prevail

Below follows a list of indicator microorganisms found in activated sludge of aeration tanks treating municipal sewage and industrial

\* These organisms can serve as indicators on the condition that they grow in sufficient quantities.

effluents. The appearance of some organisms is shown in figures (parenthesized).

The organisms found in water after bad or unsatisfactory treatment in aeration tanks.

Organisms	Sewage
<i>Beggiatoa alba</i>	Tannery
<i>Beggiatoa leptomitiformis</i>	Ditto
<i>Flagellatae</i> (colourless) (Fig. 11.26)	Municipal
<i>Amoeba limax</i> (Fig. 11.25a)	Municipal and industrial
<i>Pamphagus hyalinus</i> (Fig. 11.25h)	Municipal
<i>Paramaecium caudatum</i> (Fig. 11.27a)	Municipal and industrial
<i>Chilodon uncinatus</i>	Municipal
<i>Vorticella alba</i>	Ditto
<i>Vorticella microstoma</i> (Fig. 11.27h)	Municipal and industrial
<i>Lionotus lamella</i>	Ditto
<i>Colpidium</i> sp.	Municipal and tannery
<i>Amphileptus</i> sp.	Tannery
<i>Podophrya collini</i>	Municipal
<i>Podophrya fixa</i>	Ditto

Organisms found in water after good treatment in aeration tanks with both stages of nitrification

Organisms	Sewage
<i>Arcella</i> sp.	Industrial
<i>Euglypha</i> sp.	Ditto
<i>Lionotus fasciola</i>	Ditto
Ditto	Municipal
<i>Spirostomum teres</i>	Ditto
<i>Holophrya ovum</i>	Ditto
<i>Euplotes patella</i>	Ditto
<i>Euplotes charon</i>	Ditto
<i>Euplotes</i> sp.	Industrial
<i>Coleps hirtus</i>	Municipal
<i>Aspidisca lynceus</i>	Ditto
<i>Aspidisca turrida</i>	Industrial
<i>Aspidisca turrida</i>	Municipal
<i>Aspidisca costata</i> (Fig. 11.27b)	Ditto
<i>Carchesium polyptnum</i>	Ditto
<i>Opercularia coarctata</i> (Fig. 11.27j)	Ditto
<i>Rhabdostyla ovum</i> (Fig. 11.27f)	Ditto
<i>Urostyla weissei</i>	Ditto
<i>Vorticella convallaria</i>	Industrial
<i>Epistylis plicatilis</i> (Fig. 11.27l)	Municipal
<i>Cyclidium lanuginosum</i>	Ditto
<i>Cyclidium citrillus</i>	Ditto
<i>Cyclidium glaucoma</i> (Fig. 11.27e)	Municipal and industrial
<i>Chilodonella cocullata</i>	Municipal
<i>Lionotus lamella</i> (Fig. 11.27g)	Ditto
<i>Amphileptus claparedet</i>	Industrial
<i>Cinetochilum margaritaceum</i> (Fig. 11.27m)	Municipal
<i>Oxytricha fallax</i>	Industrial and municipal
<i>Oxytricha pellionella</i> (Fig. 11.27c)	Ditto
<i>Stylonychia pustulata</i> (Fig. 11.27d)	Ditto
<i>Tokophrya lemnae</i> (Fig. 11.28a)	Ditto
<i>Philodina roseola</i> (Fig. 11.29a)	Industrial

<i>Colurella uncinata</i>	Ditto
<i>Monostyla lunaris</i>	Ditto
<i>Monostyla cornuta</i>	Ditto
<i>Cathypna luna</i> (Fig. 11.29c)	Ditto
<i>Notommata ansata</i> (Fig. 11.29d)	Ditto
<i>Aeolosoma</i>	Ditto
<i>Vorticella convallaria</i> (Fig. 11.27i)	Ditto
<i>Opercularia glomerata</i> (Fig. 11.27k)	Ditto

In addition to the listed organisms, occur in water also round-worms *Nematodes* (see Fig. 11.30), larvae and pupa of insects (larvae of *Psychoda* and its pupa (*Podura*) and aquatic ticks, *Hydrocarina*, Fig. 13.4).

If the sewage treatment plant operates adequately, the activated sludge contains significant amounts of *Vorticella convallaria* and the colonial forms of infusoria. The motility of cilia in these organisms indicates adequate oxygenation of the tank and the absence of toxic substances in the treated sewage. The presence of *Aeolosoma* indicates stable nitrification.

The mentioned organisms are indicative of mineralization intensity since the development of each organism depends on the environmental conditions. Indicator-organisms are easily interpretable indications of the conditions at a sewage treatment plant and of the causes which interfere with its normal operation.

**Biological Ponds.** These are used for the final purification of the biologically treated sewage in all climatic conditions except frigid zones where they can be used only in summer.

Biological ponds look very much like natural water bodies (Fig. 13.5). These are artificial bodies, about 1 m deep, sizing from 0.5 to 1.5 hectare, which are connected with one another.

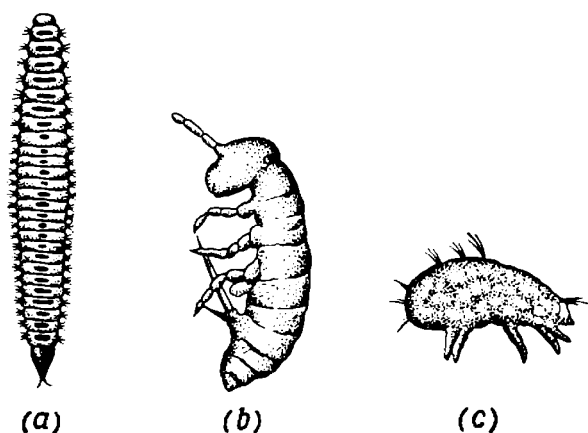


Fig. 13. Lower crustaceans:

a—*Psychoda*; b—*Podura*; c—*Hydrocarina*

Biologically treated water is filled into ponds where it is cleaned as it passes from one pond to another. The ponds are inhabited with mirror carp and ducks. They preclude the growth of duck-weeds which interfere with normal penetration of oxygen into the water.

Plankton of biological ponds is represented by thousands of minutest organisms in one millilitre and millions of bacteria (alpha- and beta-mesosaprobic bacteria). Large representatives of fauna, infusoria, rotifers, and lower crustaceans play an important role in plankton.

The function of green plankton is to produce oxygen and to provide support for microbial population. The bacterial plankton mineralizes organic substances, and zooplankton kills the bacterial plankton.

Benthos is represented in ponds by higher vegetable organisms and inhabitants of the bottom sludge, of which the most important is bloodworm. To 90,000 bloodworms live on a square metre of the bottom. The quantities of sludge which they pass daily through their bodies, 4-6 times exceed their own mass.

Plankton and benthos take an active part in the treatment of sewage. The liquid in ponds is very clear but it contains ample plankton. The treated water has low concentration of organic substances (total BOD is decreased to 5-6 mg/litre), the nitrogen of ammonium salts is contained in low concentrations as well, and the number of bacteria is meagre. The intensity of the purification process increases with rising and decreases with lowering temperature.

**Land Treatment of Sewage.** Irrigation and filtration fields are specially prepared plots of land intended for biological treatment of sewage. The liquid phase of the sewage and its nutrients are utilized to cultivate agricultural crops (sewage farms). The purpose of filtration fields is only purification of sewage, and they are loaded therefore to the maximum capacity. Sewage is fed into special furrows where it undergoes purification.

Clarified sewage undergoes complete biological purification in these fields.

Organic substances are oxidized on soils in aerobic conditions with active participation of flora and fauna.

Biocenosis of soil is composed of bacteria, fungi, algae, and animals (protozoa and invertebrates). The microbial population of

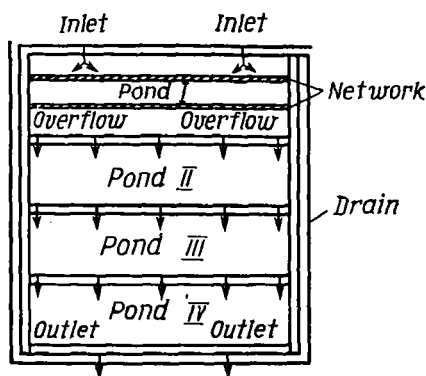


Fig. 13.5. Biological ponds

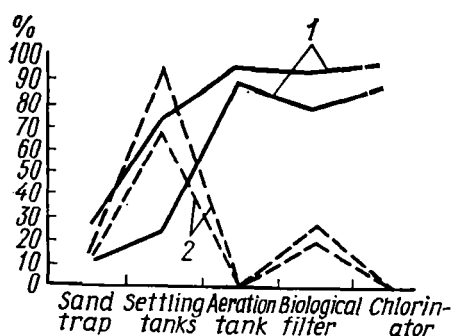


Fig. 13.6. Comparative data on destruction of the bacteria and eggs of helminths during sewage treatment:

1—bacteria; 2—helminth eggs

soil is dual in its origin. It consists of the bacterial flora of the sewage and its own bacterial flora. The microbes of these two groups are in antagonistic and symbiotic associations. Part of the microbes is killed but the remaining majority are adapted to the new conditions and actively oxidize the pollutants.

The main biochemical oxidation occurs in the upper layer of the soil (to 40 cm deep) because this layer is best of all inhabited with

microorganisms. The density of microbial population is the largest in the first ten centimeters of the soil. Here one gram of dry soil contains to  $1 \times 10^{10}$  bacteria. At a depth of 30 cm, it contains to  $2 \times 10^9$ , and at a depth of 50 cm, to  $1 \times 10^9$  bacteria.

The adsorbing power of the biological film of soil is very great, since the total surface area of the bacteria bodies on a square metre of soil is 48,000 sq. m (for 40 cm depth).

The bacteria mineralize organic substances, algae produce oxygen, and protozoa kill excess quantities of bacteria. The studies have shown that dead bacteria provide conditions for the growth of species characterized by a greater biochemical activity. Earthworms, larvae of beetles, and ticks loosen soil to facilitate the access of oxygen to heavily silted parts. Moreover, they convert stable organic substances (cellulose, chitin, keratin). Hence, in addition to bacteria, many protozoa and invertebrates also mineralize organic substances carried into soil with sewage.

The liquid treated on irrigation and filtration fields is free from helminth eggs and poor in bacteria.

**Efficiency of Aerobic Treatment of Sewage.** Of all mentioned aerobic methods of treating sewage, the land treatment is the best. The treated liquid does not contain any pathogenic microorganisms. Aeration tanks and biological filters ensure sufficient purification of water from organic substances, but they do not guarantee complete destruction of pathogenic microorganisms.

Figure 13.6 shows comparative results of microorganism retention with various water treating equipment. The oxidizing processes occurring at water treatment plants do no harm to the eggs of helminths, which are retained only in settling tanks. Biological filters retain the eggs of helminths but do not kill them. On the contrary, the conditions are favourable for their development till the invasion

stage after which they continue developing inside man or animal. Chlorination does not kill the eggs of helminths. The effective means to fight the eggs of helminths is to pass purified water through sand filters.

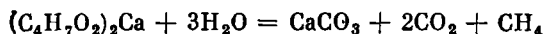
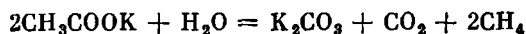
## 13.2. Anaerobic Treatment of Sewage

Anaerobic methods are used to treat sludge. The processes involved in this treatment are very complicated and induced by various anaerobic organisms. The objects of this treatment are: (1) to change the physical structure of the sludge so that it might be conveniently utilized or discarded; (2) to decrease the mass of the sludge by converting organic matter into fermentation gases and soluble salts; (3) to utilize part of organic matter in the form of the fermentation gases and the rest of the organic matter as a fertilizer.

Methane fermentation is one of the methods by which the sludge separated from sewage is treated. As has already been said, fermentation is the conversion of complicated organic substances into simpler ones. The name of the fermentation process depends on the substance which is its end product. The end product of anaerobic mineralization of sludge is methane. Hence the name.

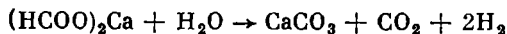
**Methane Fermentation.** The mechanism of methane fermentation was studied by many investigators. As late back as in the 18th century, the investigators noticed that a damp soil rich in organic substances liberates methane. In 1875, L. Popov studied fermentation of gum arabic to find that carbon dioxide, hydrogen and methane are formed in this process. Hoppe-Seyler observed methane fermentation of calcium salts of acetic and butyric acids in 1887. This process was accompanied by liberation of methane and carbon dioxide. The inducers of this fermentation were contained in manure.

In 1890, V. L. Omelyansky studied various biological processes in which  $\text{CH}_4$  is liberated. He also studied mineralization of salts of acetic and butyric acids by pure culture of pseudosarcine:

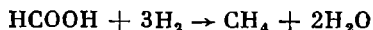


Omelyansky's experiments were followed by a systematic research of the mechanism of the formation of methane from organic and inorganic substances. The difficulty of studying methane-producing microorganisms is explained by the fact that they are anaerobes and their isolation is very difficult. Moreover, methane bacteria very slowly grow in cultures. Some investigators explain the slow devel-

opment of methane bacteria in nutrient media by the oxidation-reduction conditions. It has been established (Krasina, 1936) that the conversion of organic substances is directly dependent on the  $rH_2$  of the medium. For example, at  $rH_2$  from 12 to 12.9, calcium formate decomposes with liberation of hydrogen according to the equation:

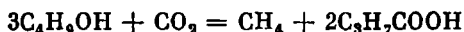
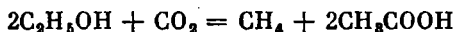
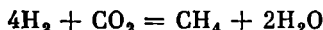


If hydrogen is introduced into the system at  $rH_2$  6-7, formic acid is mineralized to give methane:



Kuznetsov (1955) also observed decomposition of volatile fatty acids which are formed depending on the oxidation-reduction index of the medium. Volatile fatty acids are decomposed in methane tanks in thermophilic conditions (55°C) at  $rH_2$  6-8. In mesophilic conditions (32°C), this process occurs at a lower oxidation-reduction index of the medium. For example, salts of butyric acid can be fermented at  $rH_2$  1.

Many papers were dedicated to the formation of methane but it was Barker who first isolated pure cultures of bacteria (1936) which induce these processes. His method was based on the biological and biochemical properties of these species. He isolated organisms which induce the following reactions:

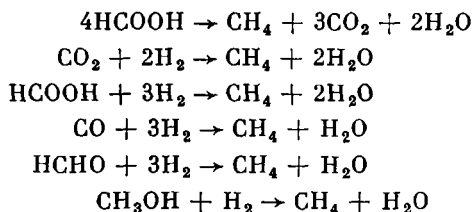


where  $\text{H}_2\text{A}$  is any compound for which a given organism has the enzyme dehydrase.

The given equations show that carbon dioxide plays an important part in the formation of methane, the former acting as the acceptor of electrons. The velocity of  $\text{CO}_2$  absorption in the first reaction depends on its concentration and attains half-maximum at  $7 \times 10^{-5}$  M. The partial pressure of  $\text{CO}_2$  being unchanged, the reaction velocity almost does not depend on pH variations in the range from 5.8 to 7.4.

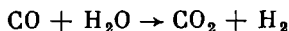
Barker used radioactive carbon in carbon dioxide to show that  $\text{CO}_2$  is reduced to methane and is consumed in the construction of cell material of methane bacteria (*Mb. omelianski* and *Methanosarcina*), which is about 1.5 per cent of the total amount of reduced carbon. Thus Barker and other investigators showed that both

aerobic and anaerobic microorganisms use  $\text{CO}_2$  for the synthesis of cell material. Stephenson and Stickland (1933) isolated an organism from river silt, whose pure culture reduced some compounds containing one carbon atom to methane. This organism had no effect on compounds which contained more than one carbon atom. Washed suspensions of this organism induced quantitatively the following reactions



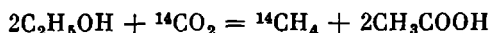
The first three reactions occur rapidly while the last three are slow reactions. The obtained information indicates that formic acid is first decomposed by hydrogenlyase ( $\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$ ) and then methane is synthesized by the second reaction.

Schnellen showed that pure cultures of two methane-forming bacteria (*Ms. barkerikerri* and *Mb. formicum*) convert CO into  $\text{CH}_4$  both in the presence and in the absence of hydrogen. If hydrogen is absent in the medium, the microorganisms oxidize CO to  $\text{CO}_2$  using the oxygen of water:



Then  $\text{CO}_2$  is reduced biochemically to  $\text{CH}_4$ .

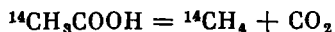
The study of pure cultures of methane-forming organisms has revealed that the mechanism of methane formation is different in each particular case, and depends on the species of the microorganisms and the substance upon which they act. For example, when grown on a medium containing ethyl alcohol, pure culture, *M. omelianskii* forms methane by reducing carbon dioxide, while ethyl alcohol is oxidized to acetic acid:



When grown on methyl alcohol medium, the culture *Methanosarcina methanica* forms the greater part of methane from carbon dioxide, but an additional reaction occurs, in which methyl alcohol is reduced to methane:



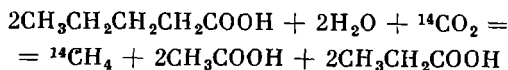
The pure culture *Methanosarcina barkerii* liberates methane from the methyl group of acetic acid:



When methane-forming bacteria act on acids having more carbon atoms than acetic acid, methane is formed by reduction of carbon

dioxide with the hydrogen of water, while the starting product forms two acids, viz. acetic acid and some other acid, whose total number of carbons is equal to the number of carbons contained in the decomposed acid.

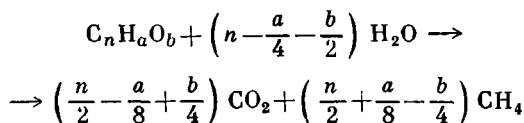
For example, when valeric acid is fermented by *M. suboxydans*, acetic and propionic acids are formed, while methane is formed from  $\text{CO}_2$ :



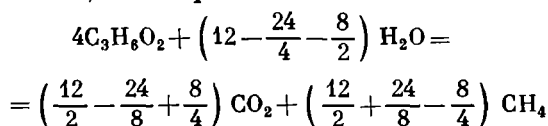
Stadtman and Barker summed up the results of the research to establish the common mechanism for the formation of methane from carbon dioxide, methyl alcohol, and acetic acid.

Water acts as an oxidizing agent in the methane fermentation; one part of the substrate molecule is oxidized while the other is reduced with hydrogen atoms to methane. The process can be described schematically as follows. A water molecule, acted upon by the enzymes, falls into hydrogen and oxygen. The hydrogen is used by microorganisms to reduce  $\text{CO}_2$  to  $\text{CH}_4$ , while the oxygen oxidizes the decarbonized radical to acid.

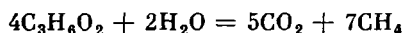
Buswell and Boruff determined the quantity of water molecules required for a given reaction with complete decomposition of an organic substance to form the gas. By analyzing the relationships between quantities of carbon, hydrogen and oxygen in the starting substance and the end products of the fermentation process, Buswell and Symons derived a universal equation by which organic substances consisting only of C, H and O are fermented in anaerobic conditions:



For propionic acid, the equation will be



or



It follows that during complete decomposition of organic substance by methane fermentation with participation of water molecules, the mass of the formed gas is larger than the mass of the organic substance involved in the process.

Table 1 in the Appendix gives the known methane-forming bacteria.

The microbiological characteristics of the methane fermentation of sewage sludge are given by Kuznetsov (1955). He studied microbiologically damp sludge loaded in the methane tank and the fermented sludge containing 95 per cent of moisture discharged from the methane tank (provided in works properly). The results are summarized in Table 13.3.

Table 13.3

Number of Living Cells in 1 g (95 per cent moisture content)

Bacteria	Sludge	
	fresh	fermented
Bacteria decomposing:		
protein	100 million	1 million
starch	50 million	1 million
cellulose	10 thousand	500 thousand
volatile fatty acids	from 50 to 500	1 million
Bacteria forming methane by reducing carbon dioxide	—	1 million

Quantitative indices of anaerobic microflora of methane tanks can deviate from the specified data depending on the composition and the size of load and temperature conditions.

The tabulated data show that the number of bacteria destroying protein and starch in the fermented sludge decreases while the number of bacteria decomposing cellulose, volatile fatty acids and methane-producing bacteria increases. The author maintains that methane is formed by mineralization of volatile fatty acids and by reduction of carbon dioxide\* with molecular hydrogen.

It should be noted that the methane-forming bacteria play an important role in the circulation of substances and the energy turnover in nature. These bacteria assimilate carbon dioxide, carbon monoxide, and hydrogen to give the hydrocarbon, methane and to synthesize their own cell substance.

The studies of methane fermentation of organic substances by the methods of chemical analysis did not give direct indications of methane origin, and it was only the method employing radioactive carbon that provided a direct proof of the fermentation mechanism. Labelled carbon atoms and the isolation of pure cultures of methane-producing bacteria helped to study the mechanism of formation

\* The research carried out at the Moscow Institute of Building and Engineering (MISI) has lead to a discovery of a method by which the mineralization of sludge in methane tanks can be accelerated by increasing the CO<sub>2</sub> concentration.

of methane from salts of fatty acids, alcohols, and other organic compounds, and by reduction of carbon dioxide and carbon monoxide with molecular hydrogen.

### 13.3. Sludge Treatment Equipment

The following equipment is used for anaerobic treatment of sewage sludge: septic tank, two-level settling tank, clarifier-destroyer\*, and methane tank. Organic matter contained in the sludge is decomposed in these units at various rates.

**Septic Tank.** This is a horizontal settling tank through which sewage is passed at a slow rate (Fig. 13.7). The sludge precipitates to the bottom and kept there for twelve months. The sedimented sludge separates with time. Part of it rises to the surface to form a floating layer. When kept for a long time, the bottom layer is compacted (to 85-88 per cent residual moisture), it starts to decay, and fermentation processes are induced in it. The evolving gases rise to the surface and trap the sediment particles with them. These particles stick to the superficial crust to increase its thickness. Various fungi grow in the upper layer and their mycelium passes through the entire thickness of the crust to strengthen it.

The floating layer keeps the heat of the unit to intensify the biological processes occurring in it. Moreover, aerobes develop

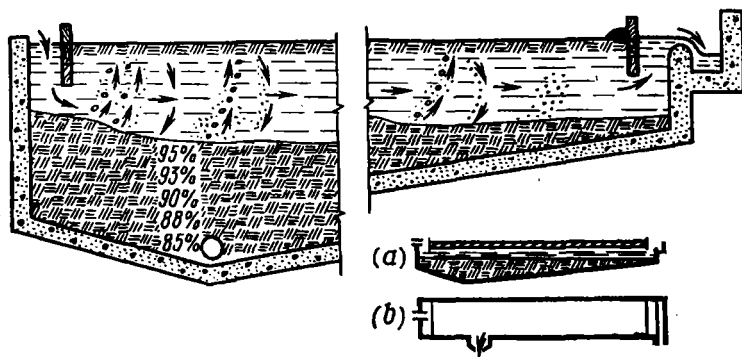


Fig. 13.7. Septic tank:

a—section; b—top view

\* The Chair of Wastewater Management at the Leningrad Institute of Building and Engineering has worked out a new unit for the primary settling of sewage and treatment of precipitated sludge. The unit was given the name "clarifier-destroyer". It is devoid of the disadvantages inherent in two-level settling tanks. The design of this new unit has been described in the book by N. F. Fedorov and S. M. Shifrin, *Sewage*, Higher School Publishers, Moscow, 1968 (in Russian).

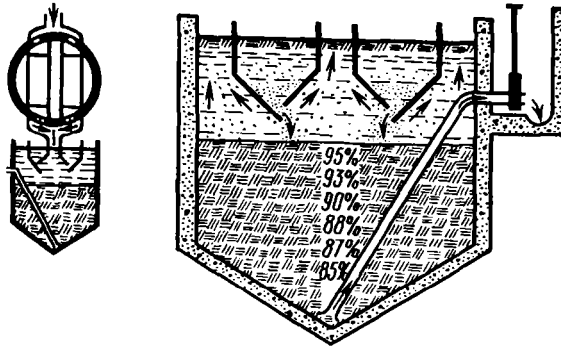


Fig. 13.8. Two-level settling tank (figures indicate moisture contents of fermented sludge)

in the crust. They absorb oxygen to ensure anaerobic conditions in the unit.

The mass of sewage moving between the crust and the sludge is enriched with the products of putrefaction, e.g. with hydrogen sulphide, and its odour becomes foul. The mixture of the sludge with the sewage does not mix well with new portions of fresh sewage and volatile fatty acids are accumulated in it to reduce the pH to 5. Therefore,  $H_2S$  is formed along with  $CO_2$ ,  $CH_4$ , and  $H_2$ .

The varied composition of the fermented sludge provides conditions for the growth of ample microflora. It has been found that one millilitre of a fermenting sludge contains billions of various bacteria.

In order to ensure mineralization of organic matter, the fermenting mass should be stirred and diluted with new portions of sewage. These conditions are not fulfilled in septic tanks since they are not provided with stirrers. The fermenting sludge accumulates the products of metabolism in concentrations harmful to microorganisms and the mineralization processes are slow. When the sludge is kept for a long time, its volume halved. The fermented sludge contains pathogenic microbes, the eggs of helminths, and cannot be used as a fertilizer. Septic tanks are used in rural sewage systems and in minor settlements.

**Two-Level Settling Tank.** This unit is shown in Fig. 13.8. Unlike in the septic tank, the sludge is precipitated in settling troughs with a longitudinal slit in the bottom through which the sludge falls into the lower septic compartment and accumulated in a 7-m deep layer. The processes occurring in the septic compartment do not differ from those in the septic tank except that the fermentation gases do not enter the passing-by sewage but are released to atmosphere as shown by arrows in the figure. The sludge does not separate in the two-level settling tank. The decomposed septic sludge is discharged

through the outlet tube under a hydrostatic pressure of 1.5-2.0 metre. When part of the bottom sludge is removed, fresh portions of sludge are added and mixed with the 'ripened' (i.e. septic) sludge. The mixture is diluted with new portions of the sewage.

Microflora of surface layers of the fermenting sludge, where the moisture content is not below 94 per cent, actively works in the two-level settling tank. (Various investigators report that the intensity of sludge decomposition weakens with decreased moisture contents.) The liquid mixture of the sewage and the sludge contains much ammonium hydrocarbonate which accounts for its high buffer capacity. The pH of the sludge mixture can therefore be maintained in the range from 6.5 to 7.8. The liberated gas has no hydrogen sulphide and the unpleasant smell is therefore absent. The decomposition in a two-level settling tank is more complete than in the septic tank because of the adequate proportion of the septic sludge and fresh portions of sewage, a better mixing, and partial renewal of sludge water during discharge of ripened sludge.

**Methane Tanks.** These are units where optimum conditions for anaerobic decomposition of organic matter of the sewage are provided.

There are numerous designs of methane tanks, but whatever it may be, the principal characteristics of this unit are the temperature of the fermenting sludge (on which the process intensity depends), the dose of fresh sludge, and the intensity of mixing of septic sludge with fresh loads.

A schematic structure of a methane tank is shown in Fig. 13.9. The unit is heated with hot water or steam. Water circulates in the tubes, while steam would be normally delivered straight into the sludge.

The contents are stirred by mechanical agitators or hydraulic pumps. Pumps would be usually used to move the bottom layers into the upper layers which loosens the fermentation mass by the liberation of ample gases. The sludge is delivered into and discharged from the tank by pumps.

Methane tanks are used for mineralization of the sludge of municipal sewage and industrial effluents containing organic matter suitable for anaerobic microorganisms.

The main condition for operation of methane tanks is the presence of septic sludge, which is heavily populated with microorganisms adapted to the given pollutants. Septic sludge is prepared during the starting period of the sewage treatment plant. To cut the time of the period, ripened sludge is taken from another (working) methane tank or from other sources, e.g. from a sewage well, since fresh sludge is fermented very slowly (to six months). If ripen and fresh sludges are taken in the proportion of 2 : 1, the microorganisms quickly become adapted to the given pollutant and the time of the starting period is thus considerably shortened.

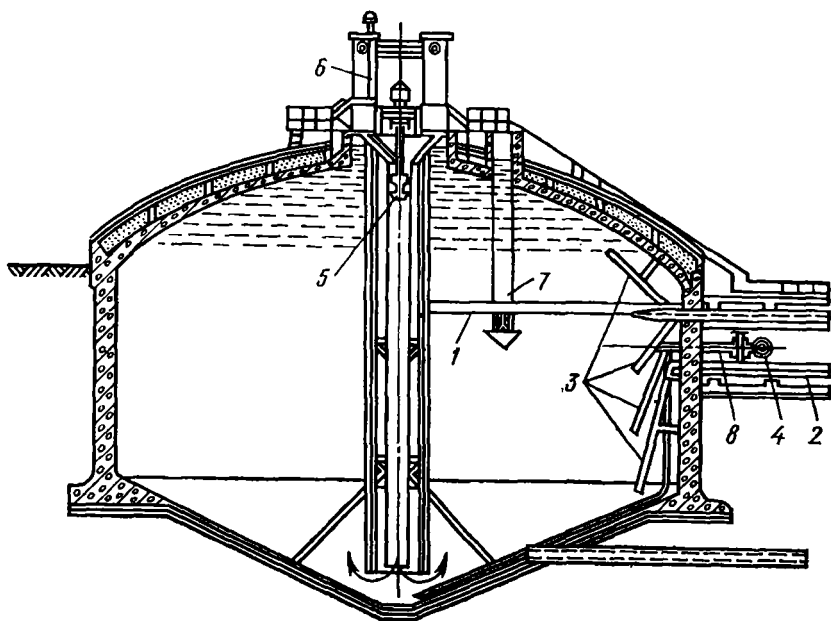


Fig. 13.9. Methane tank:

1—fresh sludge and activated sludge inlet; 2—outlet for fermented sludge from the conical part of the methane tank; 3—pipes for the withdrawal of liquefied sludge and fermented sludge from various levels; 4—steam injector (to heat fermentation mass); 5—propeller agitator; 6—gas outlet; 7—overflow pipe; 8—resistance thermometer

The starting period is accompanied by acid fermentation in which volatile fatty acids are accumulated in the sludge (see Table 13.6), the pH is decreased, and alkalinity neutralized. The whole mass has now a foul odour because of the liberation of indole, skatole, and mercaptans, and is grey. Hydrogen sulphide is now present in the gas, its methane content decreases, and the amount of carbon dioxide increases.

Fermentation in methane tanks occurs in mesophilic (from 30 to 35°C) and thermophilic (from 50 to 55°C) conditions. The optimum conditions for the process are selected with respect to the sanitary requirements and the methods of subsequent treatment and utilization.

The decomposing part of the sludge consists mainly of carbohydrates, fats, and proteins. Being treated under the same conditions, these components are mineralized at different rates and attain various degrees of decomposition during the same time. The maximum possible mineralization of sludge  $a$  (in per cent) of ashless substance is determined by the formula

$$a = (0.92_t + 0.62_c + 0.34_p) 100\%$$

Table 13.4  
Coefficients  $n$  for various moisture contents  
of sludge (%)

Fermentation temperature, °C	93	94	95	96	97
33	1.05	0.89	0.72	0.56	0.40
53	0.45	0.38	0.31	0.24	0.17

Table 13.5  
Daily Dose of Loaded Sludge with Various  
Moisture Content, %

Fermentation conditions	93	94	95	96	97
Mesophilic	7	8	9	10	11
Thermo- philic	14	16	18	20	22

Table 13.6  
Composition of Liquid Sludge

Specifications	Acid fermen- tation	Alkaline fermen- tation
pH of the medium	4.9±1.3	7.3±0.9
Volatile fatty acids, mg-equiv/litre	64.2	16.0
this figure includes:		
formic acid	13.0	4.2
acetic acid	6.0	6.2
butyric acid	45.2	5.6
Nitrogen of ammonium salts, mg/litre	144±56	270±70
Alkalinity, mg-equiv/litre	none	30

where  $f$ ,  $c$ , and  $p$  are fat, carbohydrate and protein contents, respectively, expressed in grams per gram of ashless residue.

Mineralization of ashless substance of the sludge, depending on the dose of the loaded mass, is calculated by the formula

$$y = a - nd$$

where  $y$  is the quantity of mineralized ashless substances, per cent;  $n$  is the coefficient, which depends on the moisture content of the sludge (can be found in Table 13.4); and  $d$  is the dose of the sludge, per cent (Table 13.5).

The study of the composition of the liquid sludge and gas during fermentation of both types in the methane tank of the Vasilevsky Ostrov Pumping Station of Leningrad gave the following results (Tables 13.6 and 13.7).

The changes that take place in the sludge during the methane decom-

position can be seen by comparing the specifications of fresh and fermented sludge.

Tables 13.8 and 13.9 give mean data on the composition of the sludge.

The causative agents of methane fermentation in methane tanks are the same groups of microbes which are involved in mineralization of organic substances in septic tanks and two-level settling tanks, except that in methane tanks these processes are more in-

tense because favourable conditions for the development of anaerobic microflora are provided.

The decomposition processes are the most intense in thermophilic conditions. Thermophilic organisms are characterized by very intense metabolism. Osmotic suction and excretion of wastes from the cells are faster than in mesophilic organisms. The decomposition in thermophilic fermentation is 55-65 per cent. Moreover, pathogenic microorganisms of the *E. coli* group and the eggs of helminths are destroyed in these conditions. Causative agents of typhoid fever, paratyphoid B, and dysentery are destroyed in a few hours.

The decomposition can be accelerated by adding 'concentrated biological catalysts' which are enzymes produced by bacteria decomposing organic matter to volatile fatty acids and to methane. But these 'concentrates' are quickly spent, and specially prepared bacterial culture concentrates are added. Especially effective is the addition of the sporeforming microbe *Bac. endorhynchus*, whose presence

Table 13.7

Gas Composition (% by volume)

Component	Acid fermentation	Alkaline fermentation
Hydrogen sulphide	46±16	none
Carbon dioxide	45±15	26±5
Methane	none	72±5
Ethane and higher hydrocarbons	none	none
Hydrogen	7.5±2.5	none
Nitrogen*	none	none

\* Nitrogen is of atmospheric origin and is not therefore considered. Solubilities of these gases in water are given in the Appendix, Table 3.

Table 13.8

Chemical Composition of Sludge in Primary Settling Tanks in Moscow, Leningrad, and Kharkov (per cent of dry substance)

Specification	Moscow	Leningrad	Kharkov Biological station	
	Lyublino station (average data for 1953-1954)	Sludge in radial settling tank at Vasilevsky Ostrov Pumping Station (1952)	1936	average data of 1952-1953
Moisture content	93.99	93.80	92.6	93.5
Ashless substance	77.50	66.80	72.4	67.0
Ash	22.50	33.20	27.6	33.0
Nitrogen, total	3.42	2.42	—	—
Fats	13.47	10.64	13.6	—
Carbohydrates:				
alpha-cellulose	9.08	11.04	10.2	—
hemicellulose	8.90	10.27	14.1	—

Table 13.9

Chemical Composition of Fermented Sludge  
(per cent of dry substance)

Specification	Moscow	Leningrad	Kharkov Biological Station	
	Lyublino Station (data for 1953-1955)	Sludge in methane tank of Vasilevsky Ostrov Pumping Station (1950)	1936	1952-1953
Moisture	96.4	97.2	95.6	95.8
Ashless substance	61.4	65.9	61.9	55.7
Ash	38.9	34.1	38.1	44.3
Total nitrogen	3.1	4.3	—	—
Fats	9.3	8.4	7.6	—
Carbohydrates:				
alpha-cellulose	7.2	9.1	7.3	—
hemicellulose	7.3	7.9	11.6	—
Carbon, organic	—	47.8	—	—

intensifies the formation of gases to 70 per cent. *Bac. endorhythmos* comes in symbiotic association with anaerobic microbes.

When sludge is fermented in methane tanks, one cubic metre of the solid phase gives from 10 to 18 cubic metres of gas consisting of methane (70 per cent) and carbon dioxide (30 per cent). Methane is used as fuel, while carbon dioxide for the preparation of dry ice. The solid residue, which is not destroyed by fermentation, contains mineral and organic substances required for the normal development of plants: about 12 per cent of humins, 3 per cent of total nitrogen, 3.78 per cent of phosphoric acid, 0.22 per cent of potassium oxide, and 1 per cent of calcium oxide (with respect to dry substance). The fermented sludge can be compared with the best natural fertilizers by its phosphorus and nitrogen content. Hence, the fermented sludge is used either as a fertilizer or fuel. In the latter case it is dried and bricketted.

**Control of Methane Tank Operation.** This is effected by analysing the composition of the liquid sludge, the solid phase, and gas. The liquid phase is analysed for the content of volatile fatty acids (formic, acetic and butyric acids), and for the nitrogen of ammonium salts; furthermore, the pH and alkalinity of the medium are determined.

The sludge delivered into and discharged from methane tanks is analysed for the dry substance, hygroscopic humidity, loss on ignition, fats and oils, carbohydrates (hemi- and alpha-celluloses), total nitrogen, total carbon and phosphates.

The gas is analysed for hydrogen sulphide, carbon dioxide, oxygen, hydrogen and methane.

## 13.4. Discharge of Sewage Into Sea

Sea water is colder than sewage and its density is higher. Therefore, when sewage is discharged into sea, even at a great depth, sewage floats to the surface and distributes in a thin layer over a large area. Muller (1953) derived a formula to calculate the surface area over which sewage of a settlement will be distributed:

$$S = 1.4(3.3 - P),$$

where  $S$  is the surface area of sea, in hectares, over which municipal sewage (population counting 1000) is distributed;  $P$  is the logarithm of the number of thousands of residents serviced by the given sewage system.

Sewage pollutes especially strongly the sea zone adjacent to the coast. Fats of the sewage draw a band of deposits at the tidal level. Solid particles of the municipal sewage can also be found floating on the sea surface near the shore.

The oxidation processes in sea water are less intense than in fresh water because sea water contains less oxygen:

Water temperature, °C	0	5	10	15	20	25	30
Fresh water	14.6	12.8	11.3	10.2	9.2	8.4	7.6
Sea water	11.3	10.0	9.0	8.1	7.4	6.7	6.1

Gases are known to dissolve better in pure solvent than in solutions. Oxygen enters sea water from air and due to the photosynthetic activity of algae.

Biochemical processes are slower in sea water than in river water. This is due to the osmotic phenomena which are involved in metabolism of a living cell. Nourishment is easier obtained from media containing smaller concentrations of salts. Hence the intensity of osmotic suction into the cell, which is the requisite condition for the vital processes occurring in microbes, is deteriorated in sea water.

When microbes of sewage get into sea water, they undergo drastic changes. Mineralizing microbes are killed by the unusual salts and the antagonistic action of sea water microbes. Pathogenic microflora survives in these conditions and retains its harmful properties for a long time since phytoncides produced by sea algae do not inhibit its growth.

It is recommended that these microbes should be detected by assessing the amounts of bacteriophages, whose concentration in sea water 20 times exceed the concentration of pathogenic microbes.

Pathogenic microbes infect sea fish since its intestine is a suitable medium for their growth. It follows that the biochemical self-purification of sea water is much slower, BOD decreases slower as well, while pathogenic microflora survives longer than in river water.

# APPENDICES

Table 1.

Methane-Forming Microorganisms (after N. B. Nechaeva <sup>\*</sup>, 1953)

Species	Substances from which methane is produced	Tested substances which do not give methane
<p><i>Methanobacterium söhn-genii</i> n. sp.</p> <p>This species includes:</p> <p>(a) thermophilic methane bacterium (Coolhaas, 1928)</p> <p>(b) methane bacterium (Wiken, 1940)</p>	<p>Salts of the following acids: formic, acetic, butyric, caprylic, caproic, capric</p> <p>Mixture of carbon dioxide and hydrogen</p> <p>Salts of the following acids: formic, acetic, propionic (slowly), butyric (very slowly), isobutyric, oxalic, lactic, gluconic</p> <p>Salts of the following acids: acetic, butyric, Ketones: acetone</p>	<p>Salts of the following acids: propionic, valeric, enanthic, pelargonic.</p> <p>Ethyl alcohol.</p>
<p><i>Methanobacterium omelianskii</i> n. sp.</p> <p>This species includes the second methane bacterium (Wiken, 1940)</p>	<p>Alcohols: ethyl, propyl, isopropyl, butyl, isobutyl, amyl</p> <p>Mixture of carbon dioxide and hydrogen</p> <p>Salts of formic acid</p> <p>Propyl alcohol</p>	<p>Mixtures of the following acids: formic, acetic, propionic, butyric, valeric, malonic, succinic</p> <p>Alcohols and carbohydrates: methyl, glycerol, mannitol, glucose</p> <p>Mixture of carbon dioxide and hydrogen</p> <p>Yeast autolysate</p>
<p><i>Methanobacterium formicum</i> (<i>Escherichia formica</i>)</p>	<p>In hydrogen atmosphere: formiate, formaldehyde, methyl alcohol, hexamethylene-tetraamine, carbon dioxide, or carbon monoxide</p>	<p>Compounds containing more than one carbon atom</p>

Continued

Species	Substances from which methane is produced	Tested substances which do not give methane
<i>Methanobacterium formicum</i> n. sp.	Salts of formic acid Mixture of carbon dioxide with hydrogen or water	Salts of other fatty acids
<i>Methanobacterium suboxydans</i> n. sp.	Salts of the following acids: butyric, valeric, caproic, enanthic	Salts of acetic and propionic acids
<i>Methanobacterium propionicum</i> n. sp.	Salts of propionic acid	
<i>Methanococcus mazei</i> n. sp. this species includes: (a) coccus (Groenwege) (b) coccus (Wiken)	Salts of acetic and butyric acids  Salts of acetic acid Butyrate and acetone	Ethyl and butyl alcohols
<i>Methanococcus vannielii</i> n. sp.	Formiates, mixture of carbon dioxide and hydrogen	Salts of the following acids: acetic, propionic, butyric, succinic. Alcohols: methyl and ethyl Carbohydrates: glucose
<i>Methanosarcina methanica</i>  This species includes <i>sarcina</i> (Wiken)	Salts of acetic and (possibly) butyric acids Methyl alcohol Salts of acetic, propionic and butyric acids	Ethyl alcohol
<i>Methanosarcina barkeri</i> n. sp.	Salts of acetic acid (difficult), methyl alcohol, mixture of carbon dioxide with hydrogen or water	Salts of other organic acids and other alcohols

\* Nechaeva, N. B., Formation of Methane by Microorganisms. *Microbiology*, vol. XXII, issue 4, p. 457, 1953 (in Russian)

### Solubility of Gases in Water and Salt Solutions

The solubility of gases in solutions of salts decreases with growing concentration of the salt. The quantitative expression of this regularity is expressed by Sechenov's equation:

$$N' = N \times 10^{-Kn} \quad \text{or} \quad \log \frac{N'}{N} = -Kn$$

where  $N'$  and  $N$  are the gas components, in mole fractions, of mineralized and pure water, respectively;  $n$  is the salt concentration in solution, in g-equiv/litre;  $K$  is the coefficient of Sechenov's equation (salting out coefficient), depending on the nature of gas and dissolved salt, temperature, and pressure.

Tables 2, 3, 4 and 5 give solubilities of gas in millilitres per litre of solution. If volumes are to be converted into weight units, the number of millilitres of dissolved gas should be multiplied by the coefficient 0.713 for methane, 1.383 for oxygen, 1.250 for nitrogen, and 1.964 for carbon dioxide. The result will be expressed in milligrams per litre.

For example, 48.7 ml of methane has dissolved in one litre of water at 5°C. Express the gas content in milligrams per litre:

$$48.7 \times 0.713 = 34.72 \text{ mg/litre}$$

Table 2

Solubility of Methane in Water and Sodium Chloride Solutions at Various Temperatures and Partial Pressure of Gas of 760 mm Hg (ml/litre)

Temperature, °C	NaCl concentration, g-equiv/litre												
	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.4	K
5	48.7	40.3	32.8	26.6	22.0	18.0	14.8	12.2	10.0	8.4	6.9	5.8	0.172
10	42.1	35.2	29.2	24.3	20.2	17.0	14.0	11.7	9.7	8.1	6.8	5.8	0.159
15	37.2	31.6	26.4	22.2	18.8	15.9	13.5	11.3	9.5	7.8	6.6	5.8	0.148
20	33.3	28.3	24.1	20.4	17.5	14.8	12.7	10.8	9.2	7.8	6.6	5.8	0.140
25	30.4	26.0	22.2	19.0	16.3	14.0	12.0	10.3	8.9	7.6	6.5	5.8	0.133
30	27.5	23.8	20.5	17.6	15.3	13.1	11.4	9.8	8.5	7.4	6.4	5.7	0.127
35	25.3	22.0	19.1	16.6	14.4	12.5	11.0	9.5	8.2	7.2	6.2	5.6	0.122
40	23.9	20.8	18.2	15.9	14.0	12.1	10.6	9.2	8.0	7.0	6.1	5.5	0.118
45	22.7	20.0	17.5	15.3	13.4	11.8	10.3	9.0	7.9	7.0	6.1	5.5	0.114
50	21.7	19.1	16.8	14.8	13.0	11.4	10.1	8.8	7.8	6.9	6.0	5.5	0.111
55	20.8	18.4	16.2	14.3	12.6	11.2	9.9	8.7	7.7	6.8	6.0	5.4	0.108
60	20.2	17.8	15.8	14.0	12.4	10.9	9.7	8.6	7.6	6.7	6.0	5.4	0.106
65	19.6	17.4	15.4	13.7	12.2	10.7	9.5	8.4	7.5	6.7	5.9	5.4	0.104
70	19.2	17.0	15.1	13.4	11.9	10.6	9.4	8.3	7.4	6.7	5.9	5.3	0.102
75	18.8	16.7	14.9	13.2	11.8	10.5	9.4	8.3	7.4	6.6	5.9	5.2	0.101

Note: The solubility of gas is expressed here in ml of methane (at 0°C and 760 mm Hg) saturating one litre of solution, i. e. in Bunsen coefficients,  $\alpha \times 10^3$ . The Bunsen coefficient is the volume of a gas (in ml) at 0°C and 760 mm Hg, dissolved in 1 ml of solvent if the pressure of this gas over liquid is 760 mm Hg.

Table 3

Solubility of Carbon Dioxide in Water and Sodium Chloride Solutions at Various Temperatures and Partial Pressure of 760 mm Hg (in ml/litre)

Temperature, °C	NaCl concentration, g-equiv/litre												K*
	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.4	
0	1713	1489	1293	1124	1018	894	785	689	605	531	466	420	$K_1$ 0.122 $K$ 0.113
5	1432	1251	1093	956	871	769	679	600	530	468	413	374	$K_1$ 0.117 $K$ 0.108
10	1195	1051	923	811	737	653	578	512	454	402	357	324	$K_1$ 0.112 $K$ 0.105
15	1005	889	785	694	634	565	504	449	400	357	318	290	$K_1$ 0.107 $K$ 0.100
20	870	774	688	612	559	500	448	401	359	322	288	264	$K_1$ 0.101 $K$ 0.096
25	757	675	601	536	495	446	401	361	324	292	262	241	$K_1$ 0.100 $K$ 0.092
30	665	597	537	482	433	389	350	314	282	254	228	209	0.093
35	593	533	480	432	388	349	314	282	254	229	205	189	0.092
40	527	474	427	385	346	312	281	253	228	205	185	170	0.091
45	475	428	386	348	314	283	255	230	207	187	168	155	0.090
50	434	391	353	320	289	258	233	210	189	171	154	142	0.090

\* To decrease the error, it is reasonable to use the following Sechenov equation coefficients:  $K_1$ —for salt concentrations from 0.5 to 2.0 g-equiv/litre,  $K$ —for salt concentrations from 2.0 to 5.4 g-equiv/litre.

Table 4

Solubility of Nitrogen in Water and Sodium Chloride Solutions at Various Temperatures and Partial Pressure of Gas of 760 mm Hg (in ml/litre)

Temperature, °C	NaCl concentration, g-equiv/litre												K
	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.4	
10	19.5	16.2	13.5	11.2	9.3	7.7	6.4	5.3	4.5	3.8	3.1	2.7	0.160
15	17.4	14.7	12.4	10.4	8.8	7.4	6.3	5.3	4.4	3.7	3.2	2.8	0.148
20	16.0	13.7	11.7	10.0	8.5	7.3	6.2	5.3	4.5	3.9	3.3	2.9	0.137
25	14.8	12.8	11.0	9.5	8.1	7.0	6.1	5.2	4.5	3.9	3.4	3.0	0.129
30	13.8	12.0	10.4	9.1	7.9	6.9	6.0	5.2	4.5	3.9	3.4	3.1	0.121
35	12.8	11.2	9.8	8.5	7.5	6.5	5.7	5.0	4.4	3.8	3.3	3.0	0.117
40	12.2	10.7	9.4	8.3	7.2	6.4	5.6	4.9	4.3	3.8	3.3	3.0	0.113
45	11.5	10.1	9.0	7.9	7.0	6.1	5.4	4.8	4.2	3.7	3.3	3.0	0.109
50	11.3	10.0	8.8	7.8	6.9	6.1	5.4	4.8	4.3	3.8	3.3	3.0	0.106
55	11.1	9.8	8.7	7.7	6.8	6.0	5.3	4.7	4.2	3.7	3.3	3.0	0.106
60	10.8	9.6	8.5	7.5	6.6	5.9	5.2	4.6	4.1	3.6	3.2	2.9	0.106
65	10.7	9.5	8.4	7.4	6.6	5.8	5.1	4.6	4.0	3.6	3.2	2.9	0.106
70	10.6	9.4	8.3	7.4	6.5	5.8	5.1	4.5	3.9	3.5	3.1	2.8	0.106

Note: The irregular changes in nitrogen solubility with growing temperature can be explained by superimposition of errors in calculations and experiment procedure with small absolute values of solubility.

Table 5

Solubility of Oxygen in Water and Sodium Chloride Solutions at Various Temperatures and Partial Pressure of Gas of 760 mm Hg (in ml/litre)

Temperature, °C	NaCl concentration, g-equiv/litre												
	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.4	K
0	48.9	39.8	32.1	26.3	21.4	17.4	14.1	11.5	9.2	7.6	6.2	5.2	0.180
5	42.9	35.4	29.1	24.0	19.8	16.3	13.4	11.1	9.1	7.5	6.2	5.3	0.168
10	38.5	32.0	26.6	22.2	18.4	15.3	12.8	10.6	8.8	7.3	6.1	5.3	0.160
15	34.2	28.6	23.9	20.2	16.7	13.9	11.6	9.7	8.1	6.8	5.7	4.9	0.156
20	30.8	25.9	21.9	18.4	15.5	13.1	11.0	9.3	7.8	6.6	5.5	4.8	0.149
25	28.2	23.9	20.2	17.1	14.5	12.2	10.4	8.8	7.4	6.3	5.3	4.7	0.145
30	26.3	22.5	19.1	16.3	13.9	11.8	10.0	8.6	7.3	6.2	5.3	4.7	0.139

### Mathematical Treatment of Physico-Chemical Data

The theory of errors regards two types of errors: constant and random.

Constant errors are those which do not practically change during the experiment. The sources of constant errors are (1) errors due to defective or faulty instruments; (2) errors connected with the environmental conditions; (3) errors due to inaccuracy of universal constants; (4) errors due to subjective features of the experimenter; (5) errors introduced by the method itself because of the approximate character of theoretical relationships between the observed values and the values of special concern of the experimenter.

Constant errors depend on the particular apparatus used in the experiment and the method, and therefore there is no special theory accounting for these errors. But if the source of error is identified, its effect on the desired value can be assessed.

Random errors are associated with the factors which undergo insignificant changes during the experiment. For example, the results of weighing on analytical balances depend on many factors, including vibration of the balance pans, inconstancy of illumination of the working post, changes in the organs of senses of the experimenter, etc. The action of this multitude of factors, which are often difficult to control, gives different readings when one procedure is repeated several times.

Mathematical statistics treats random errors from the standpoint of the theory of probability. The dependence of random errors ( $\mathcal{E}_{\text{random}}$ ) on the number of determinations  $n$  can be expressed as follows:  $\mathcal{E}_{\text{random}} = 1/\sqrt{n}$ . Hence, a random error diminishes with increasing number of determinations.

The classification of errors as constant and random is only conventional and holds true for a given experiment with a great number of determinations.

Mathematical statistics offers the following sequence of calculations to find a random error:

1. The results of an experiment obtained by multiple determinations in the same conditions are entered into the second column of Table 6.

2. All experimental data are summed up and an arithmetic mean is found from the formula

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n \bar{x}_i$$

where  $n$  is the number of determination;  $\bar{x}$  is the arithmetic mean.

3. The difference between the result of each determination and the arithmetic mean is found  $(x_i - \bar{x})$ . The result is entered into the third column in Table 6.

4. The occasional variance  $n$  of found random values of  $x$  is expressed in mathematical statistics by the expression

$$s^2(x) = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2$$

therefore, the difference between each determination and the arithmetic mean is raised to the second power and the result is written in the fourth column of the Table 6. The sum of squares is substituted into the formula  $s^2(x)$ .

5. A square root is now extracted from  $s^2(x)$  dispersion to obtain the value of  $s(x)$ , the general mean quadratic or standard deviation (error).

6. The random error is found from the formula characterizing the confidence limits of integral for the given probability  $\alpha$ :

$$\mathcal{E}_{\text{random}}(x) = \frac{t_{1-\alpha}(f) s(x)}{\sqrt{n}}$$

where  $n$  is the number of determinations;  $f$  is the number of degrees of freedom;  $t_{1-\alpha}$  is the function of density of distribution probability, which depends only on the number of degrees of freedom  $f$  of dispersion  $s^2(x)$ . The value of  $t_{1-\alpha}(f)$  can be found in tables\*.

**Example.** Find a random error for determination of the velocity constant of mineralization of organic matter in municipal sewage.

1. The velocity constants for mineralization of organic matter during five days are determined experimentally (see column 2, Table 6).

Table 6  
Error of Determination

Number of determinations	$k_i$	$k_i - \bar{k}$	$(k_i - \bar{k})^2$
$k_1$	0.2300	+0.0012	0.00000144
$k_2$	0.2253	-0.0035	0.00001225
$k_3$	0.2307	+0.0019	0.00000361
$k_4$	0.2288	0.0000	—
$k_5$	0.2292	+0.0004	0.00000016
$\Sigma$	1.1440		0.00001746

2. Determine the mean value of the velocity constant,  $\bar{k} = 0.2288$ .

3. Find the difference between each value of the constant and its arithmetic mean  $(k_i - \bar{k})$  and raise to the second power  $(k_i - \bar{k})^2$ .

\* Spiridonov, V. P. and Lopatkin, A. A., *Mathematical Treatment of Physico-Chemical Data*, Moscow University Press, 1970, appendix 2 (in Russian).

4. Determine the occasional variance of a random value from the formula

$$s^2(k) = \frac{1}{5-1} \sum (k_i - \bar{k})^2 = \frac{17.46 \times 10^{-6}}{4} = 4.36 \times 10^{-6}$$

5. Determine the general mean-square deviation (error)

$$s(k) = \sqrt{4.36 \times 10^{-6}} = 2.09 \times 10^{-3}$$

6. Assume  $a = 0.95$ ,  $f = 5 - 1 = 4$  for the confident probability; in Table 7 find  $t_{0.95}(4) = 2.7764$ ,  $\sqrt{5} = 2.236$ , and determine the random error from the formula

$$\mathcal{E}_{\text{random}}(k) = \frac{t_{1-a}(f) s(k)}{\sqrt{n}} = \frac{2.7764 \times 2.09 \times 10^{-3}}{2.236} = 0.0026$$

Hence,  $k = 0.2288 \pm 0.0026$ .

### Determining Possible Range of Random Value

If the probability  $a$  for a random value  $t$  to be found within a certain range is given, the borders of the sought range will be characterized by the values  $-t_{1-a}(f)$ ,  $+t_{1-a}(f)$ , which depend on the number of degrees of freedom  $f$  and the given  $p$  [ $-t_{1-a}(f) < t_{1-a}(f)$ ] =  $a$ .

In order to determine the values of  $t_{1-a}(f)$  Table 7 gives the values of  $t_p(f)$  for probabilities  $p = 0.5, 0.25, 0.1, 0.05, 0.025, 0.01, 0.005$  and degrees of freedom  $f = 1, 2, 3, \dots$ .

Table 7  
Values of  $t_p(f)$

$f$	$p$						
	0.50	0.25	0.10	0.05	0.025	0.01	0.005
1	1.0000	2.4142	6.3138	12.7060	25.452	63.6570	127.32
2	0.8165	1.6036	2.9200	4.3027	6.2053	9.9248	14.089
3	0.7649	1.4226	2.3534	3.1825	4.1765	5.8409	7.4533
4	0.7407	1.3444	2.1318	2.7764	3.4954	4.6041	5.5976
5	0.7267	1.3009	2.0150	2.5706	3.1634	4.0321	4.7733
6	0.7175	1.2733	1.9432	2.4469	2.9687	3.7074	4.3168
7	0.7111	1.2543	1.8946	2.3646	2.8412	3.4995	4.0293
8	0.7064	1.2403	1.8595	2.3060	2.7515	3.3554	3.8325
9	0.7027	1.2297	1.8331	2.2622	2.6850	3.2498	3.6897
$\infty$	0.6745	1.1503	1.6449	1.9600	2.2414	2.5758	2.8070

**Graphical Representation of Experimental Data.** The results of determinations are collected in tables where each value of one parameter  $x$  corresponds to a definite value of the other parameter  $y$ . Graphs are often constructed on these data. The scale for the axes of coordinates should be selected so that the graph should be a square, i.e. so that the distance between the extreme points on the axis of ordinates and the axis of abscissas should be about the same. If a graph is a straight line, it should be so located that the angle of inclination

should be close to  $\pm 45^\circ$ . This is a general rule which should be observed for the sake of convenience.

The method of least squares is often used to treat experimental data. If there is a linear dependence between the parameters, the equation  $y = mx + b$  is used. The slope of the straight line is determined by the value of  $m$ , while the distance on the axis of ordinates, by the value of  $b$ :

$$m = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}; \quad b = \frac{\sum x^2 \sum y - \sum x \sum xy}{n \sum x^2 - (\sum x)^2}.$$

To determine  $m$  and  $b$ , the experimental data are represented in the form of a table of five columns:  $n$ ,  $x$ ,  $y$ ,  $x^2$  and  $xy$ , where  $n$  is the number of determinations;  $x$  and  $y$  are experimental data;  $x^2$  and  $xy$  are obtained by calculations. All values in each column are summed up to obtain the sums  $\sum n$ ,  $\sum x$ ,  $\sum y$ ,  $\sum x^2$ , and  $\sum xy$ . The values of  $m$  and  $b$  are found by substituting the summary values into the above equations.

Consider the changes in the oxidation-reduction potential  $rH_2$  of natural fresh water depending on a 5-day BOD.

*Solution.*  $x = \text{BOD}_5$  and  $y = rH_2$

$n$	$x$	$y$	$x^2$	$xy$
1)	5.28	24.4	27.88	128.83
2)	3.61	25.7	13.03	92.77
3)	3.20	26.4	10.24	84.48
4)	2.26	26.5	5.10	59.89
5)	2.71	27.1	7.35	73.44
$\sum = 5$	17.0	130.1	63.6	439.4

Find:

$$m = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2} = \frac{5 \times 439.4 - 17 \times 130.1}{5 \times 63.6 - 17^2} = \frac{14.7}{29} = -0.5$$

$$b = \frac{\sum x^2 \sum y - \sum x \sum xy}{n \sum x^2 - (\sum x)^2} = \frac{63.6 \times 130.1 - 17 \times 439.4}{5 \times 63.6 - 17^2} = 27.7$$

Hence  $y = -mx + b = -0.5x + 27.7$ .

With  $x_1 = 0$ ;  $y_1 = 27.7$

$x_2 = 1$ ;  $y_2 = -0.5 \times 1 + 27.7 = 27.2$

$x_3 = 2$ ;  $y_3 = -0.5 \times 2 + 27.7 = 26.7$

$x_4 = 3$ ;  $y_4 = -0.5 \times 3 + 27.7 = 26.2$

$x_5 = 4$ ;  $y_5 = -0.5 \times 4 + 27.7 = 25.7$

$x_6 = 6$ ;  $y_6 = -0.5 \times 6 + 27.7 = 24.7$

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